NC STATE University

CHEMICAL REACTIVITY IN SOIL MICROSITES

The Need for Rapid, High-Resolution, Multi-Element Synchrotron X-ray Capabilities

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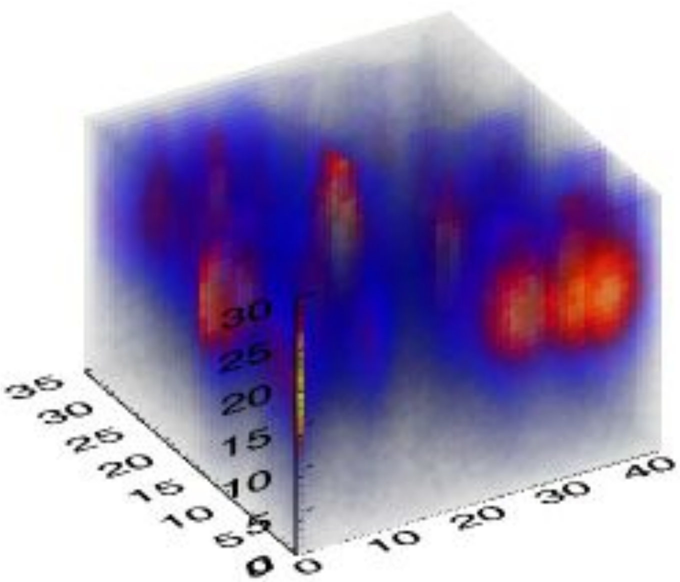
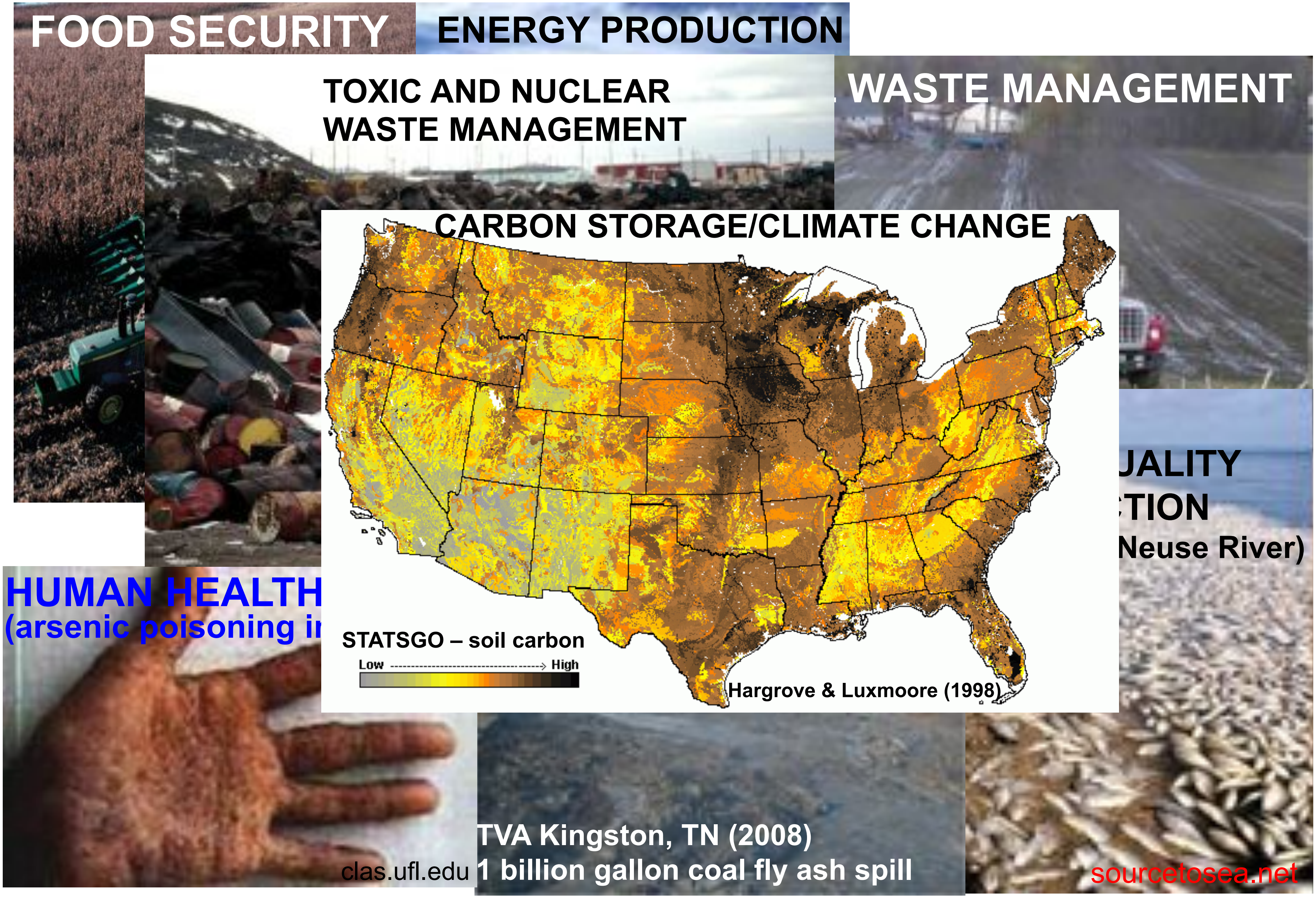


COLLABORATORS

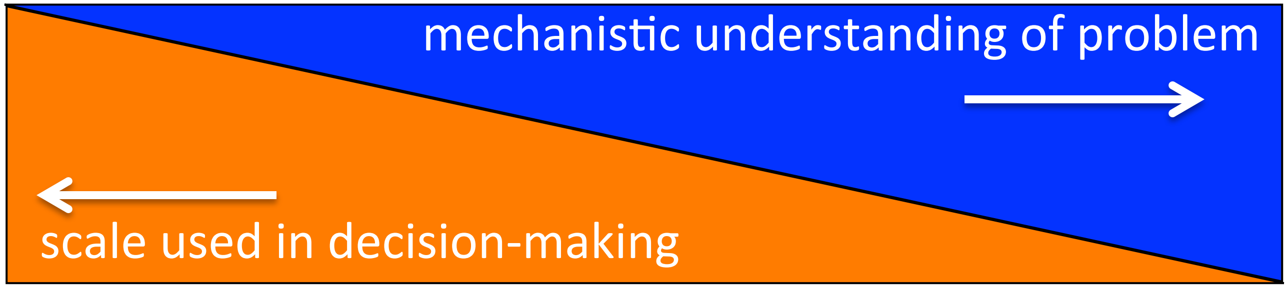
Ryan Tappero and Paul Northrup (NSLS)
Ian McNulty (APS)
Juergen Thieme (NSLS-II)

ROCK & CELL – EARLY SCIENCE WORKSHOP NSLS-II

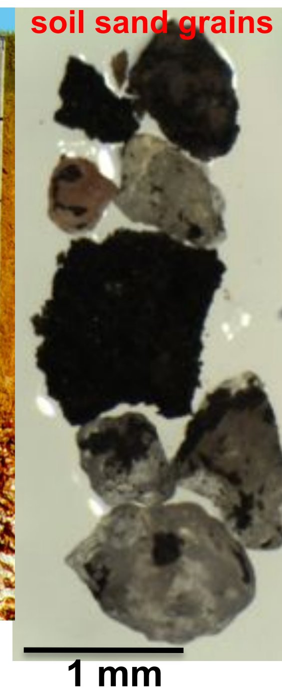
COMPETING DEMANDS ON OUR SOIL RESOURCES

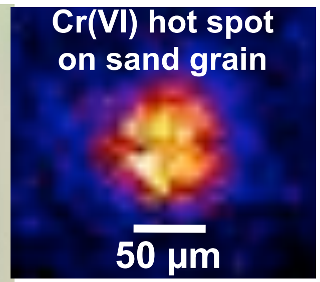


MOLECULAR ENVIRONMENTAL CHEMISTRY AND LAND MANAGEMENT

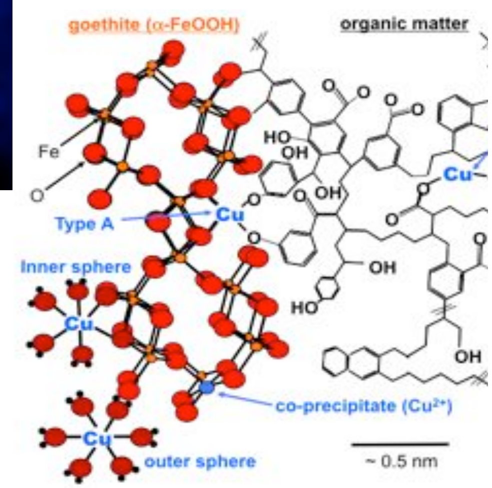


kilometer | meter | millimeter | micrometer | nanometer





molecular-binding
mechanisms of copper



Hesterberg et al. (2011)

energy production
toxic waste management
precision agriculture

soil classification
reactive chemical transport modeling

Knowledge transfer?

OBJECTIVE

Illustrate limitations and opportunities for applying synchrotron x-ray micro/nanoprobes to soil materials.

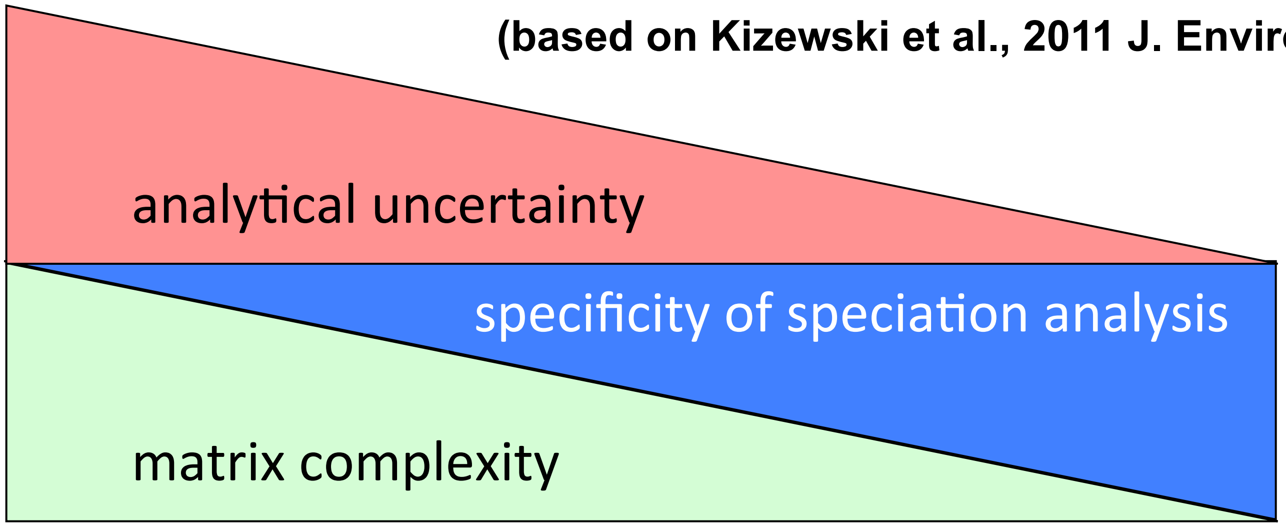
CHEMICAL REACTIVITY IN SOIL MICROSITES

- The Chemical Speciation Model
- The Reactive Microsite Model
- Measuring Soil Reactivity

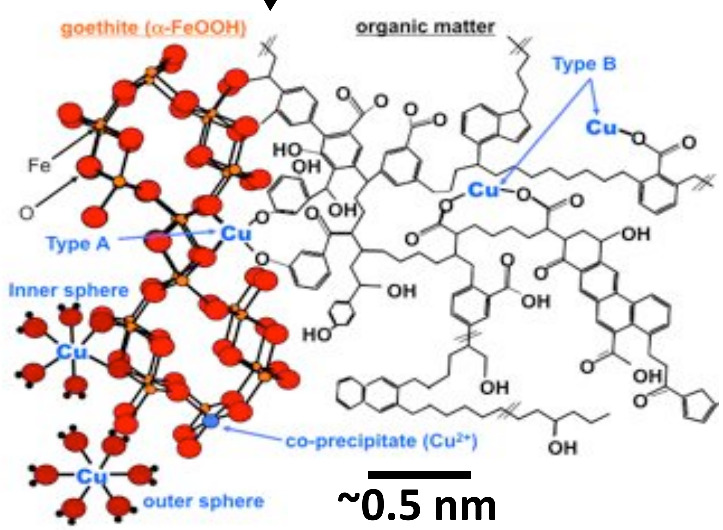
The Chemical Speciation Model

SOIL COMPLEXITY AND ANALYTICAL SPECIFICITY

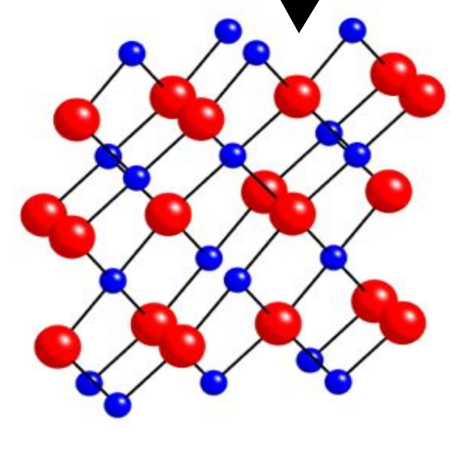
(based on Kizewski et al., 2011 J. Environ. Qual. 40:751)



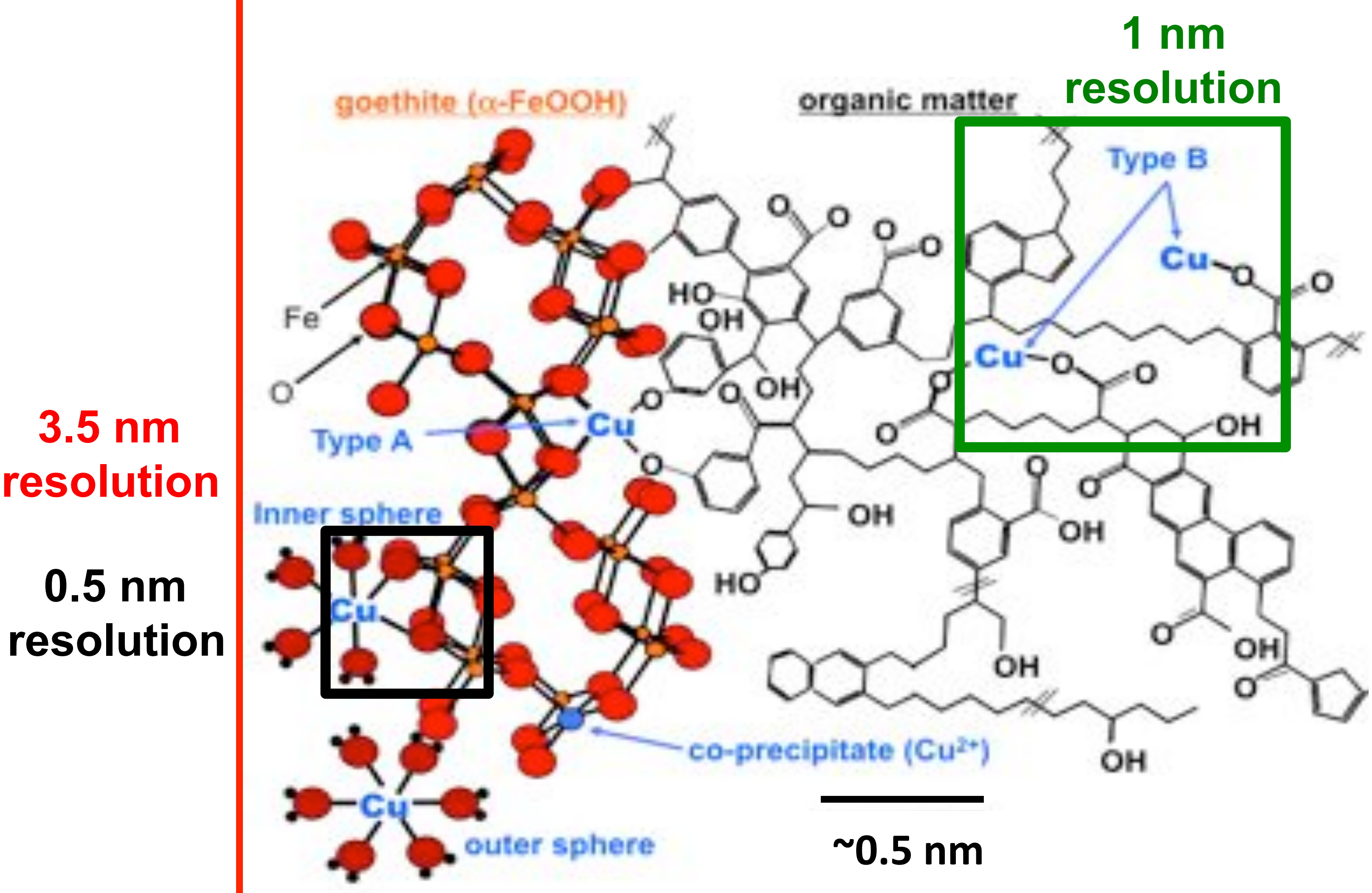
soil/ sediment | natural organic matter | bio-molecules | non-crystalline solids | model systems (e.g., mineral-adsorbed species) | minerals/ crystalline compounds



tenorite (CuO)



ANALYTICAL SPECIFICITY



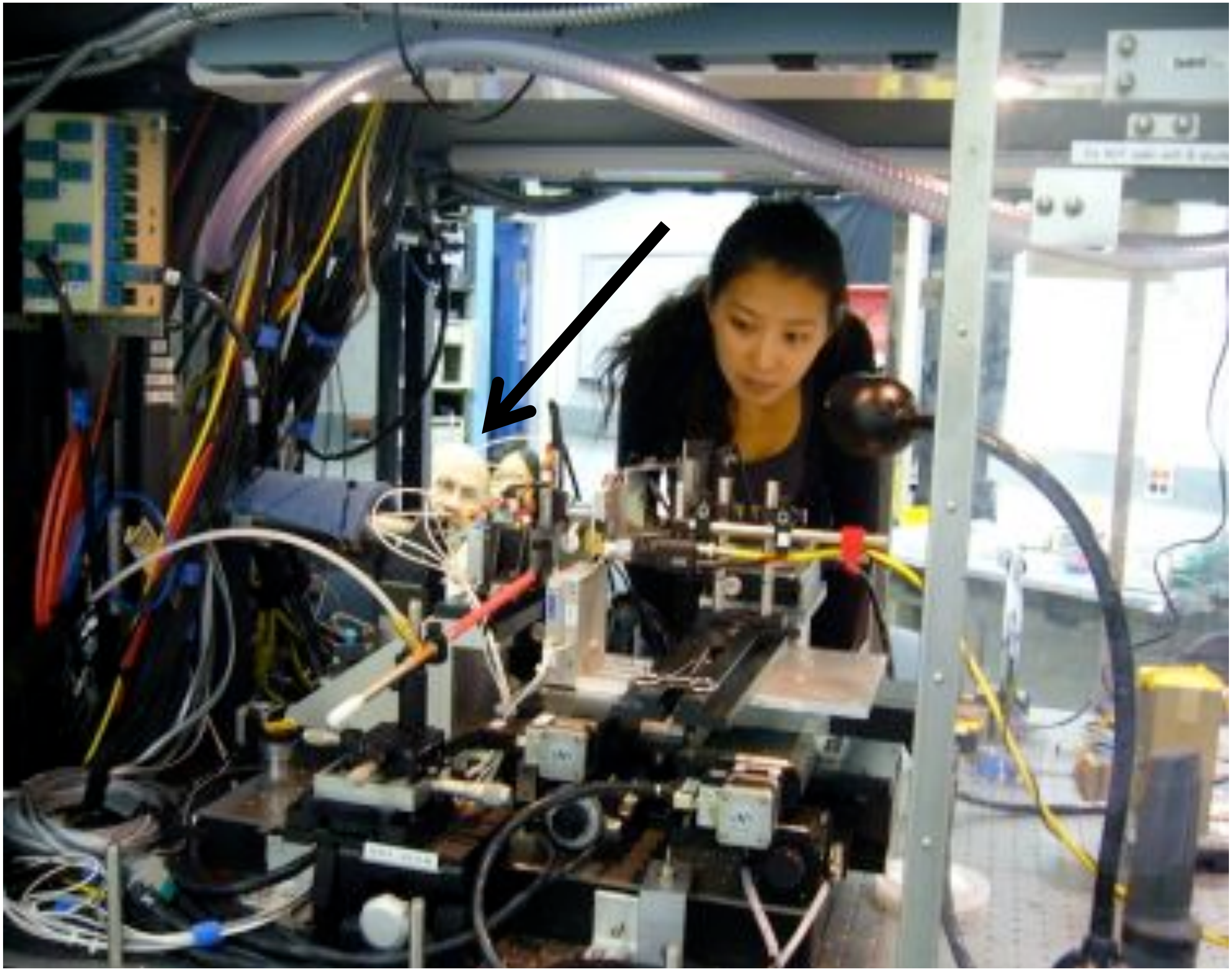
(based on Hesterberg et al., 2011 J. Environ. Qual. 40:667)

Those are species found in different model systems, but how many different chemical species of an element are in a given soil?

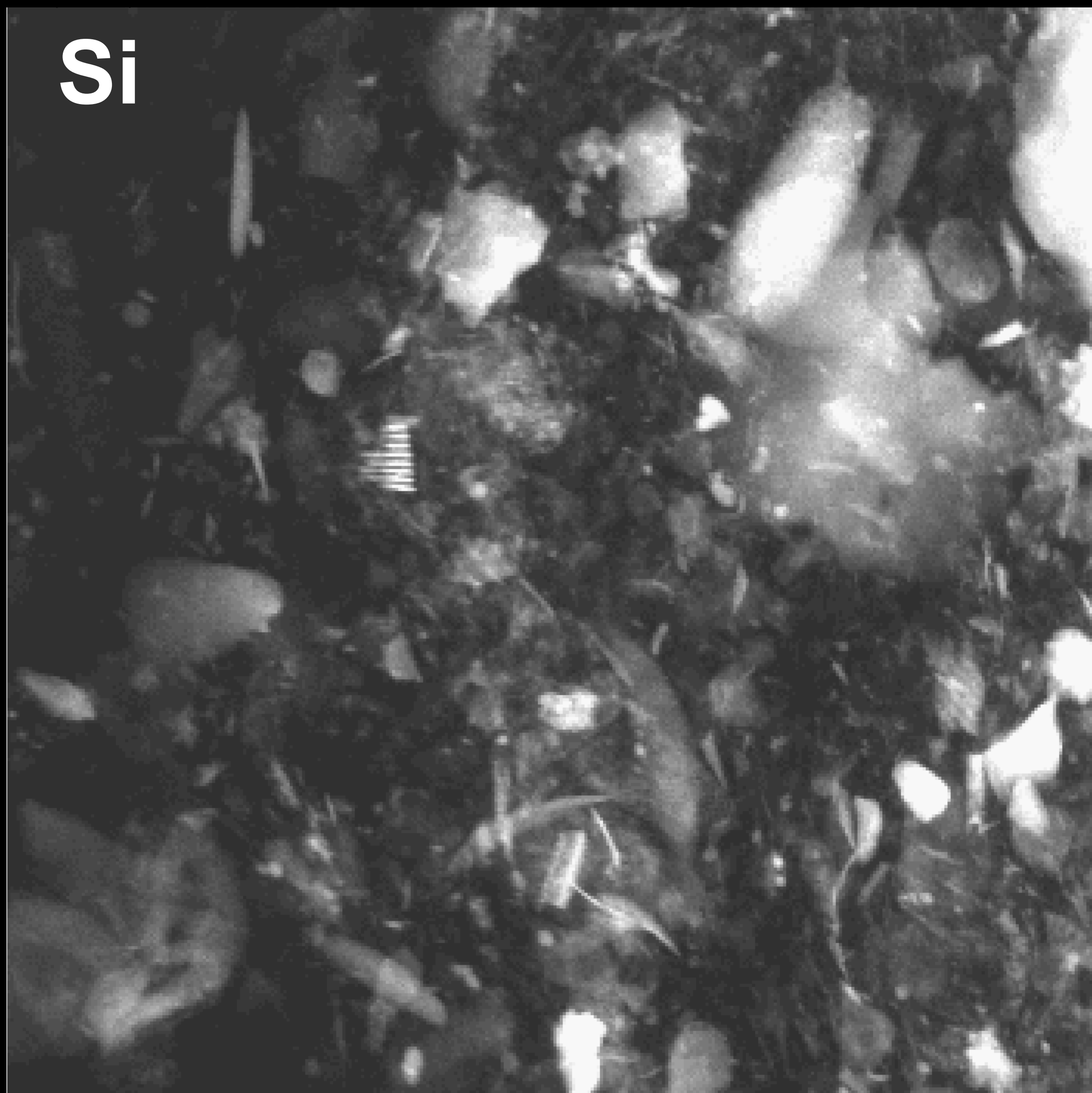
PHOSPHORUS EXAMPLE

Balancing Phosphorus Nutrition and Water Quality

APS Sector 2-ID-B X-ray Microscope



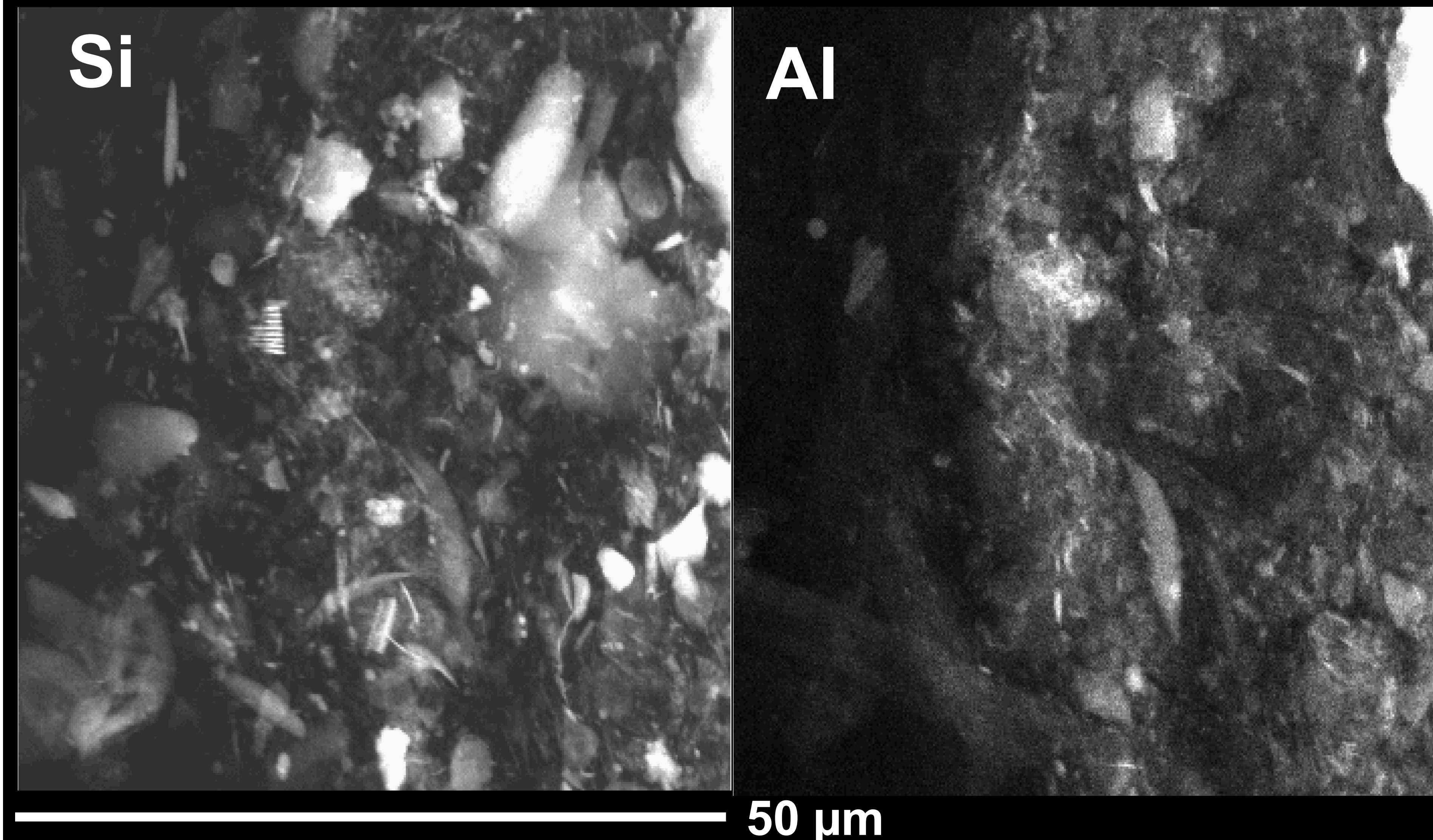
Silicon Map – Organic Soil Sample from North Carolina



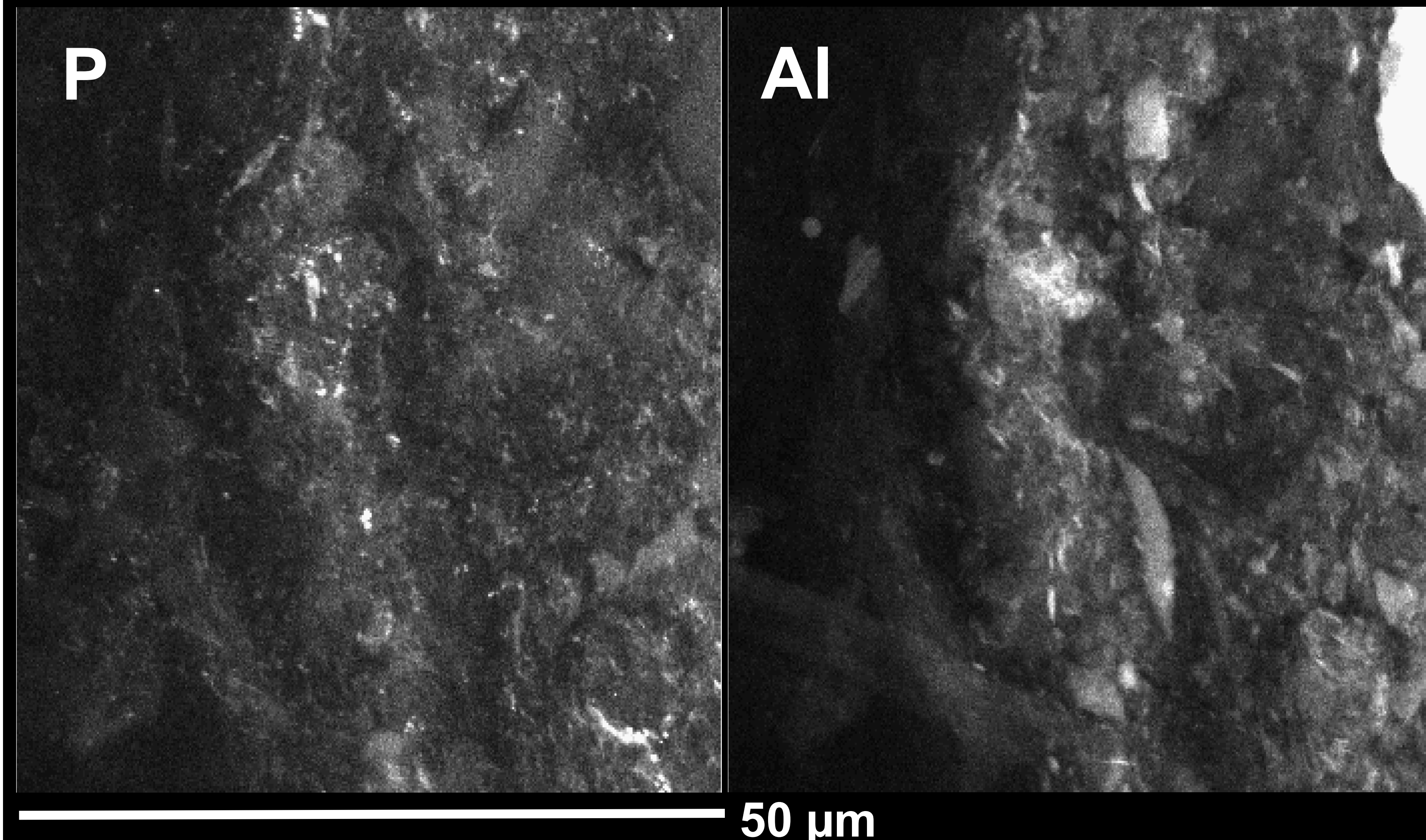
50 µm

(30 nm spot size)

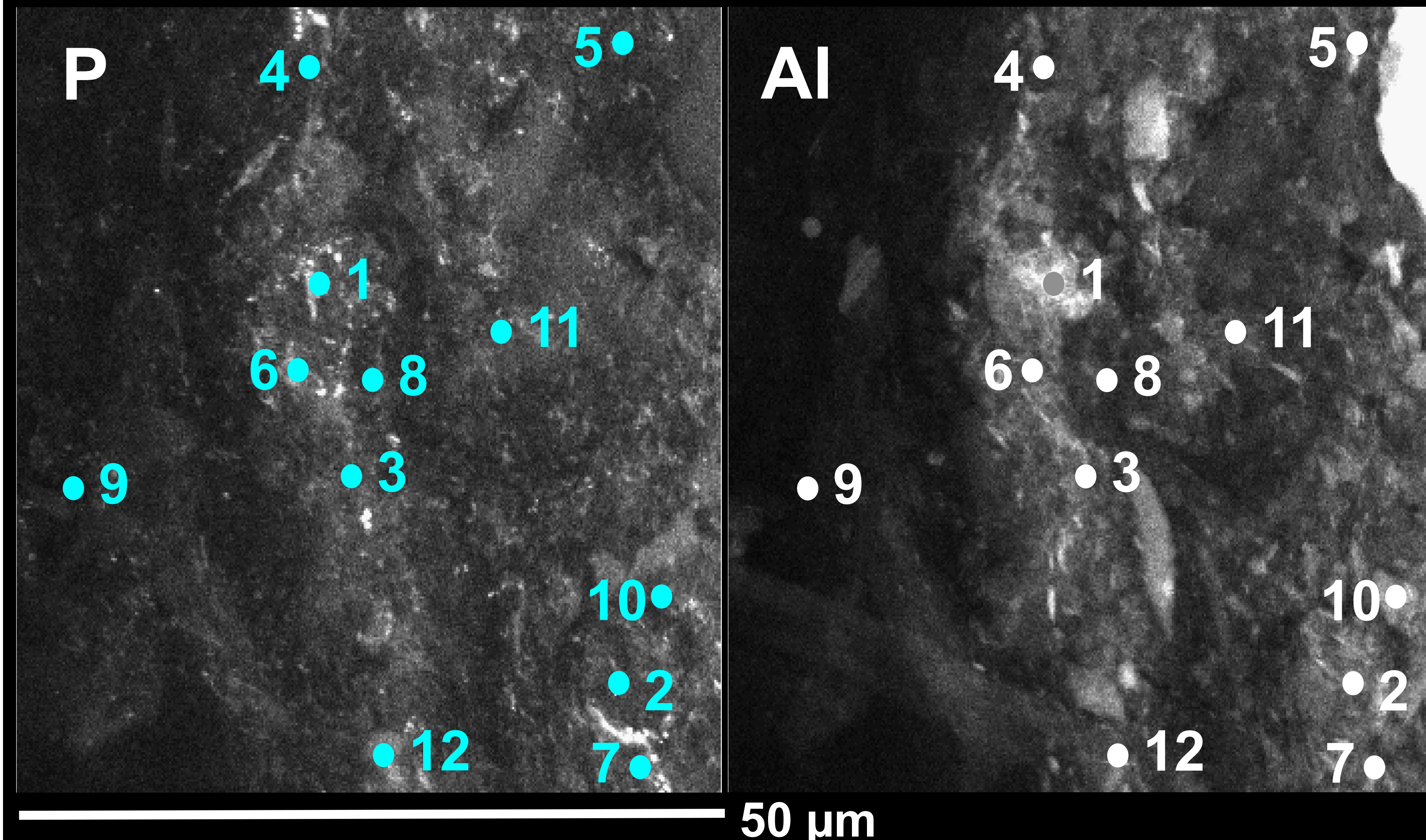
SILICON AND ALUMINUM MAPS



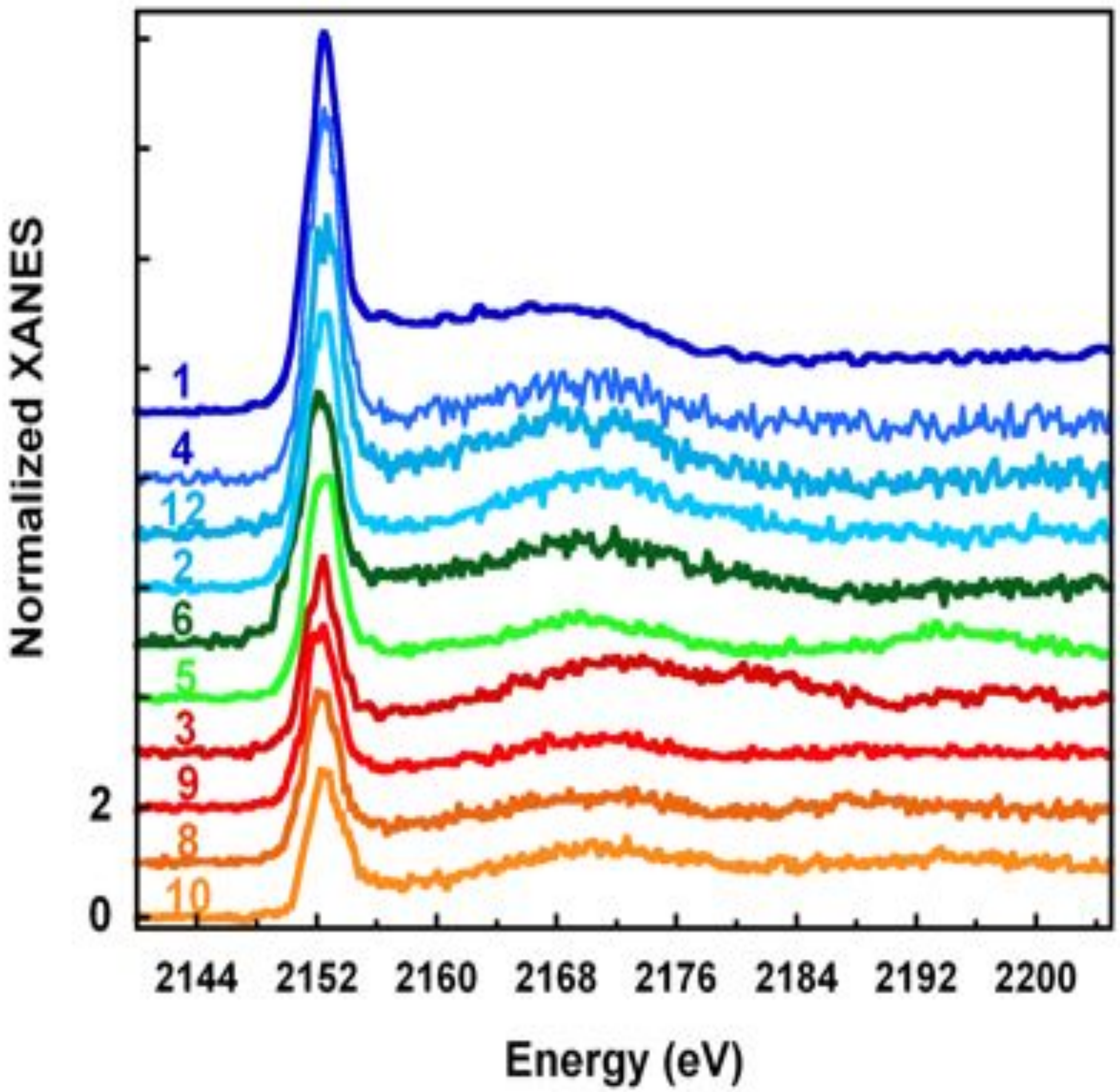
PHOSPHORUS AND ALUMINUM MAPS



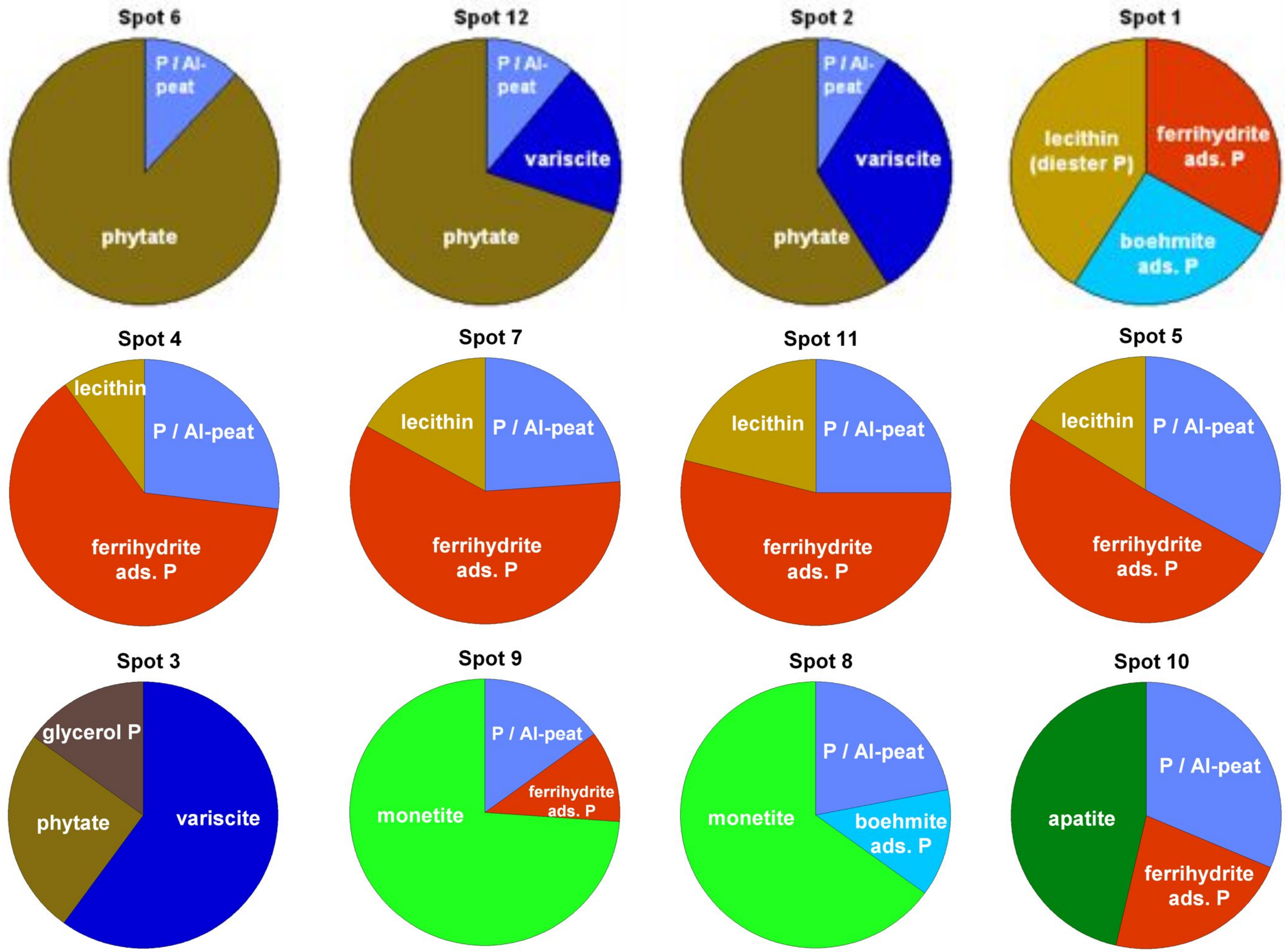
PHOSPHORUS AND ALUMINUM MAPS



Diversity of P K-edge XANES spectra within a 50 x 50 µm area of organic soil material

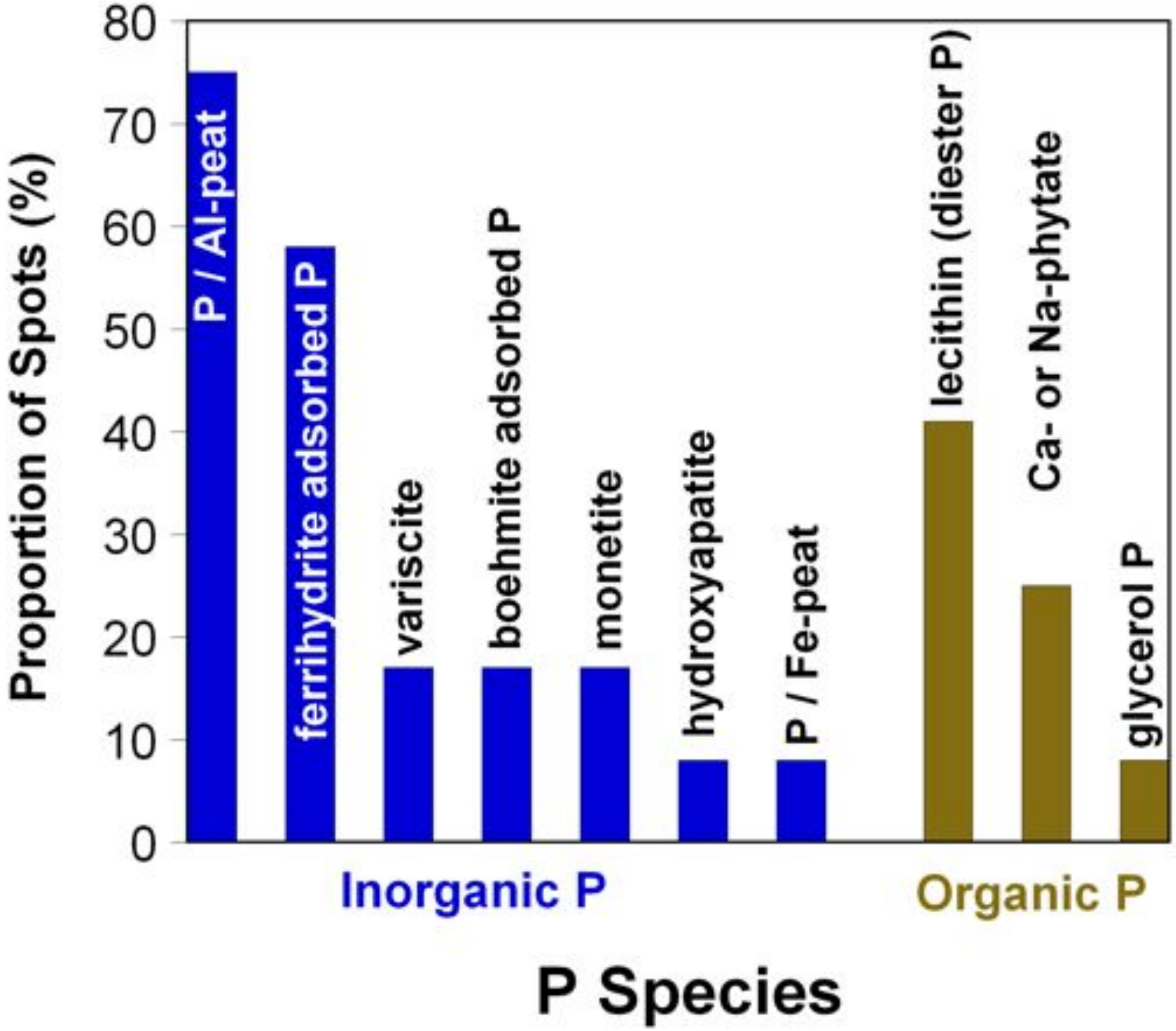


Overall P Species Distribution (50 x 50 µm Sample Region)



Fits to P XANES spectra in 50 x 50 μm^2 region included ten standards.

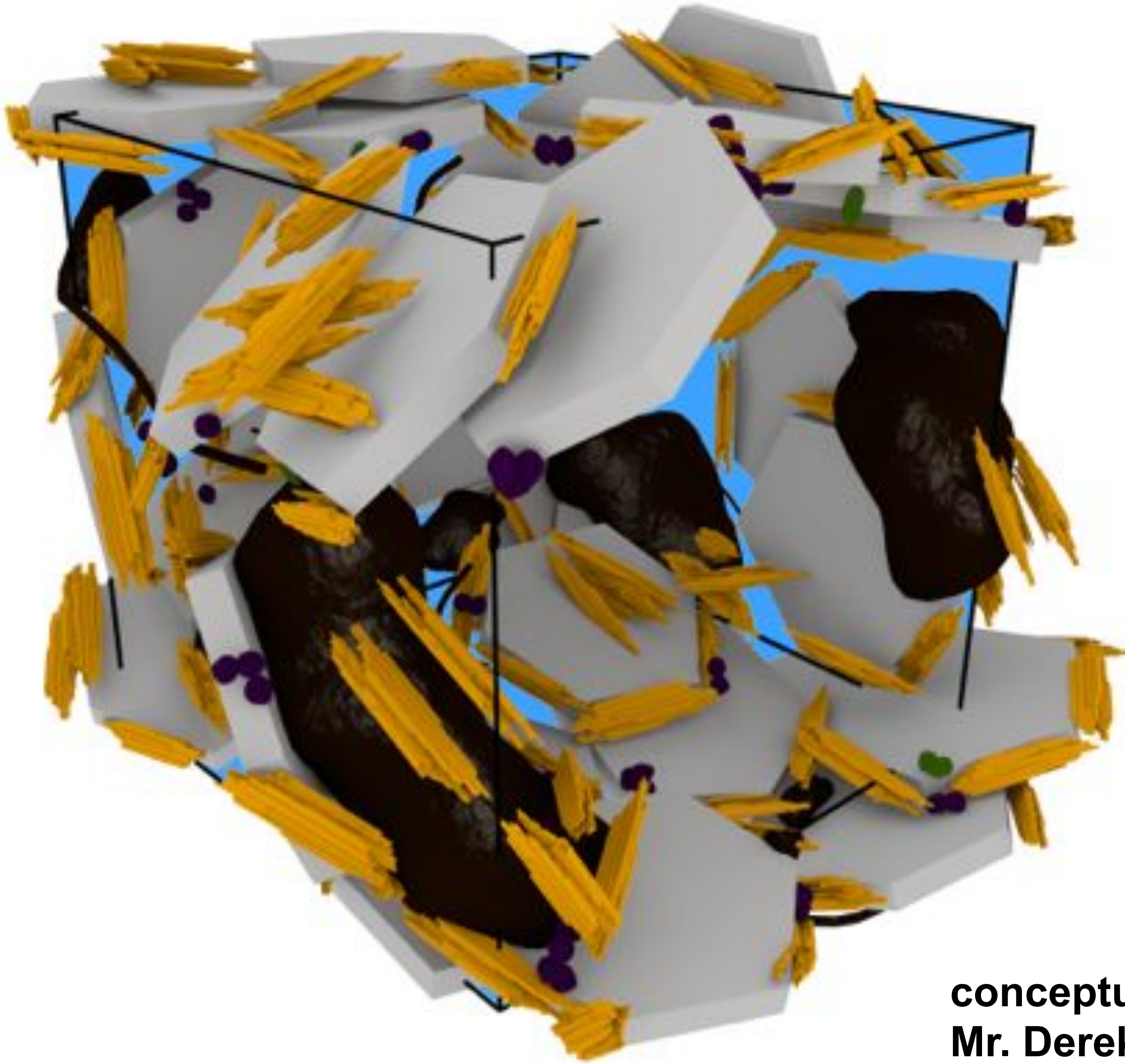
How mobile is phosphorus in this soil?



THE REACTIVE MICROSITE MODEL

Hypothesis: Need chemical speciation AND geochemical microenvironment properties to predict mobility

1 μm^3



conceptual model drawn by
Mr. Derek Elliot

CHEMICAL TRANSFORMATIONS WITHIN SOIL MICROSITES OF VARYING COMPOSITION MIGHT INFER DOMINANT REACTION MECHANISMS

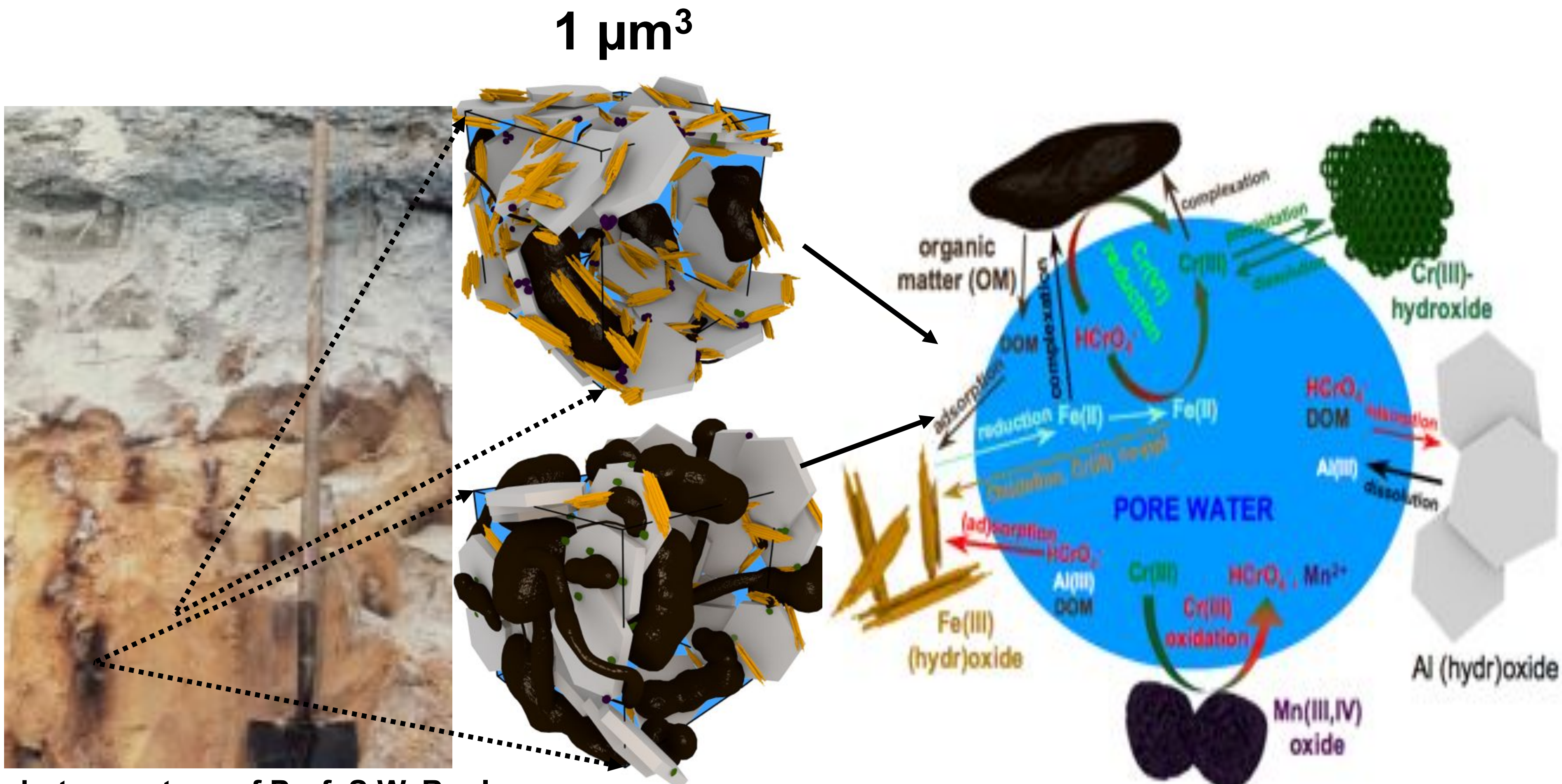
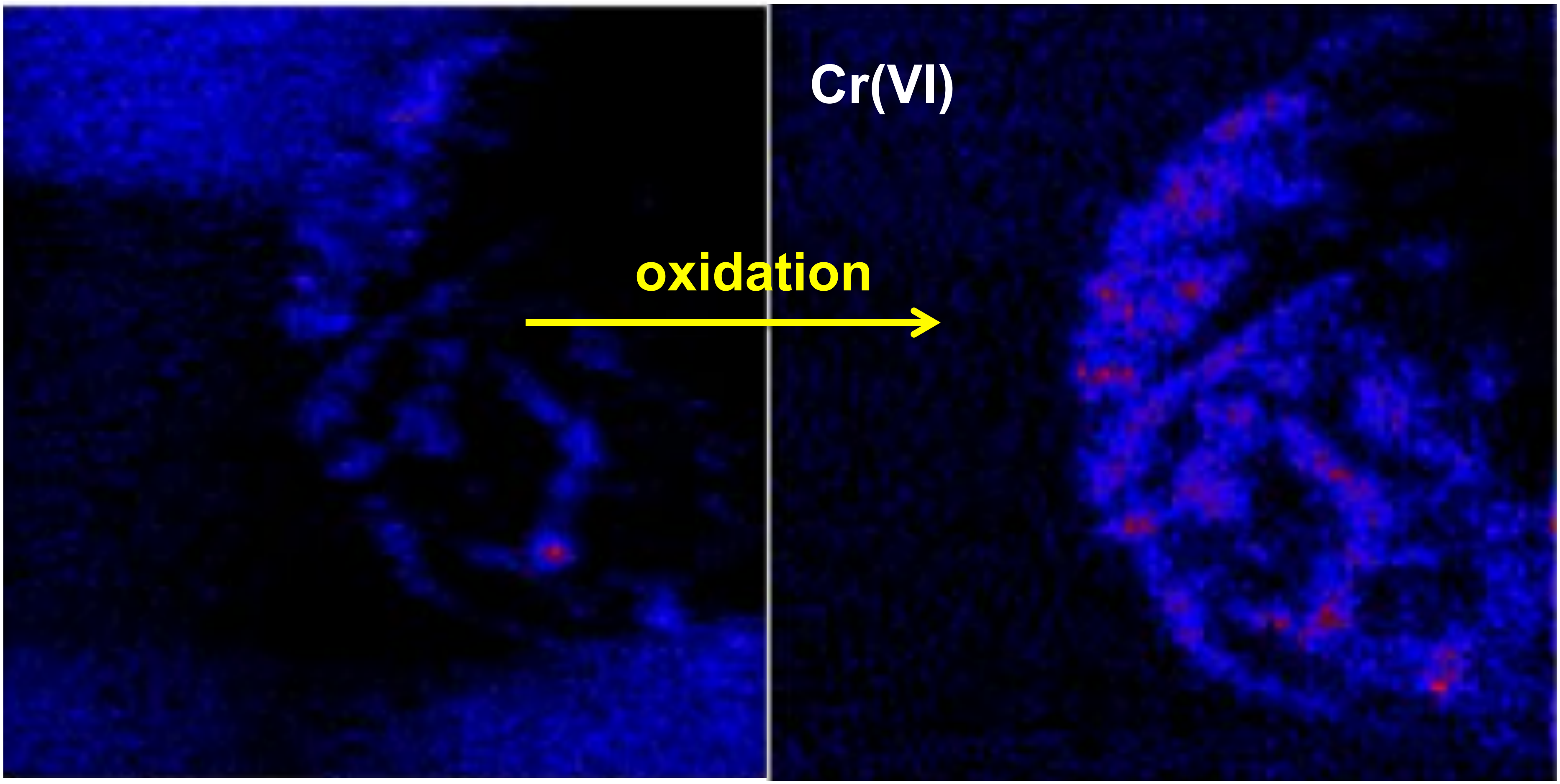


photo courtesy of Prof. S.W. Buol

(based on Hesterberg et al., 2011 J. Environ. Qual. 40:667)

conceptual models drawn
by Mr. Derek Elliot

MEASURING MICROSCALE SOIL REACTIVITY

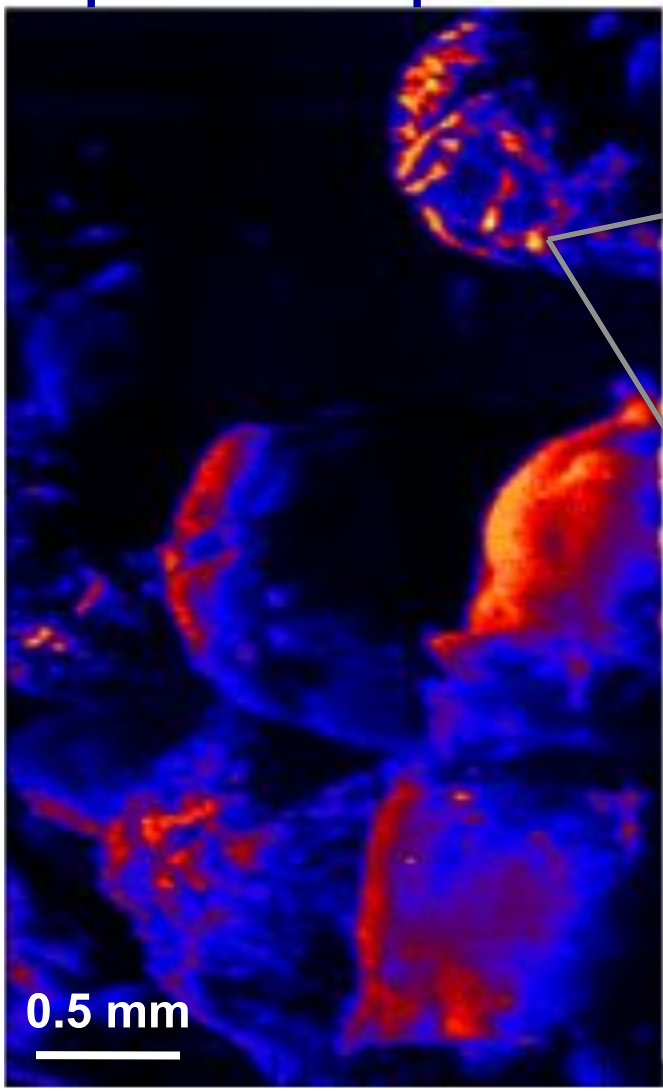


EXAMPLE

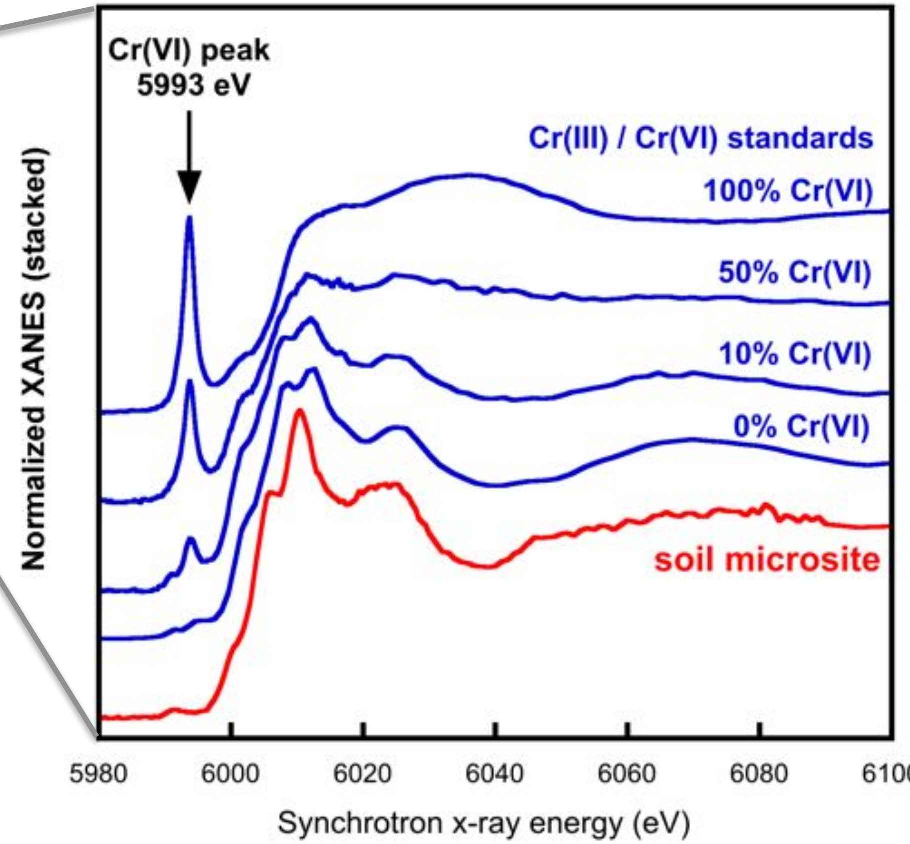
OXIDATION OF NATURALLY OCCURRING CHROMIUM IN A SERPENTINIC SOIL

MICROSCALE Cr SPECIATION IN SERPENTINIC SOIL MATERIAL

Chromium distribution in serpentinic soil particles



Chromium(VI) not detected by micro-XANES analysis of selected spots

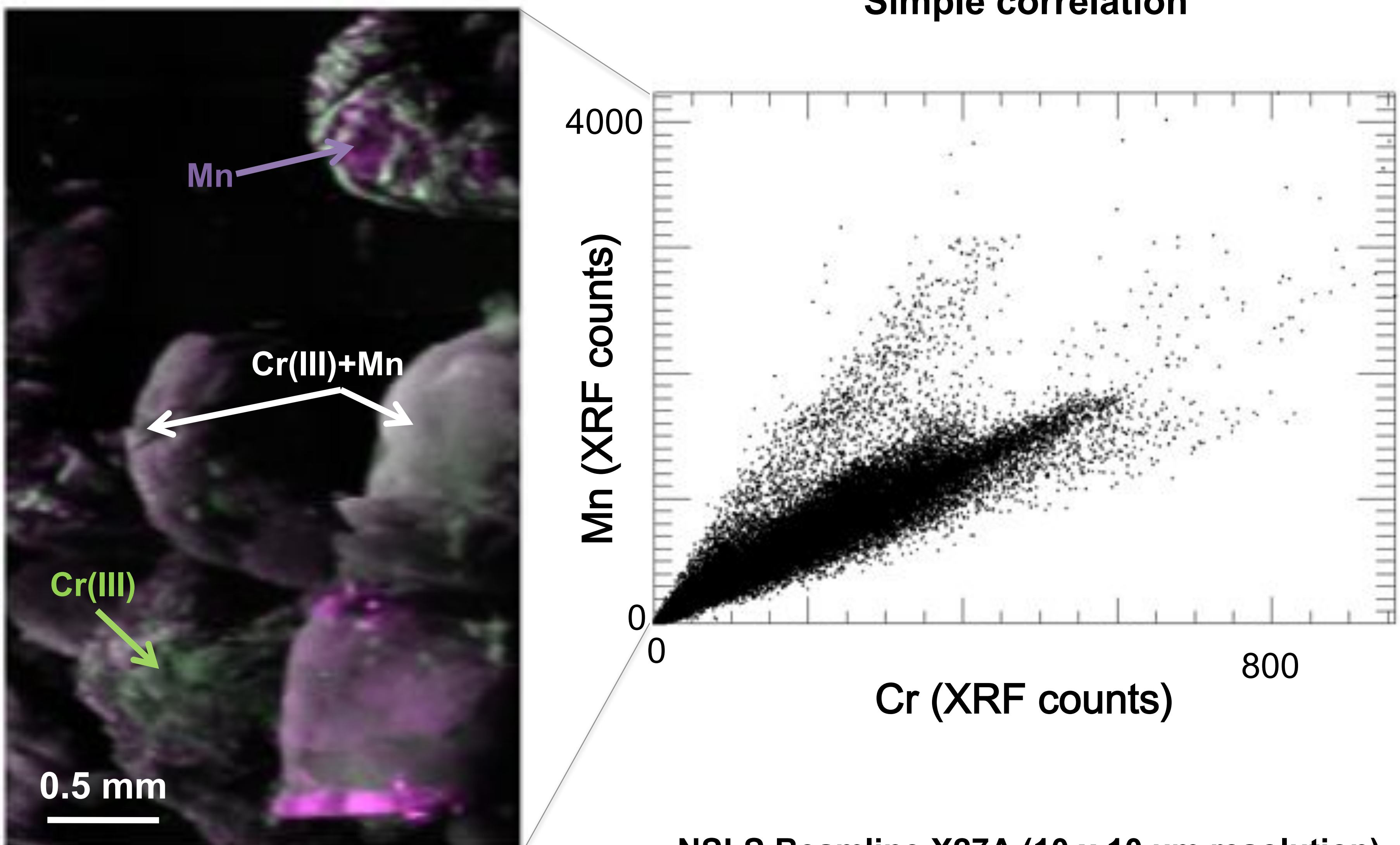


NSLS Beamline X27A (10 x 10 μm resolution)

GEOCHEMICAL MICROENVIRONMENT PROPERTIES OF SOIL MATERIAL

Co-localization of chromium and manganese (known redox couples)

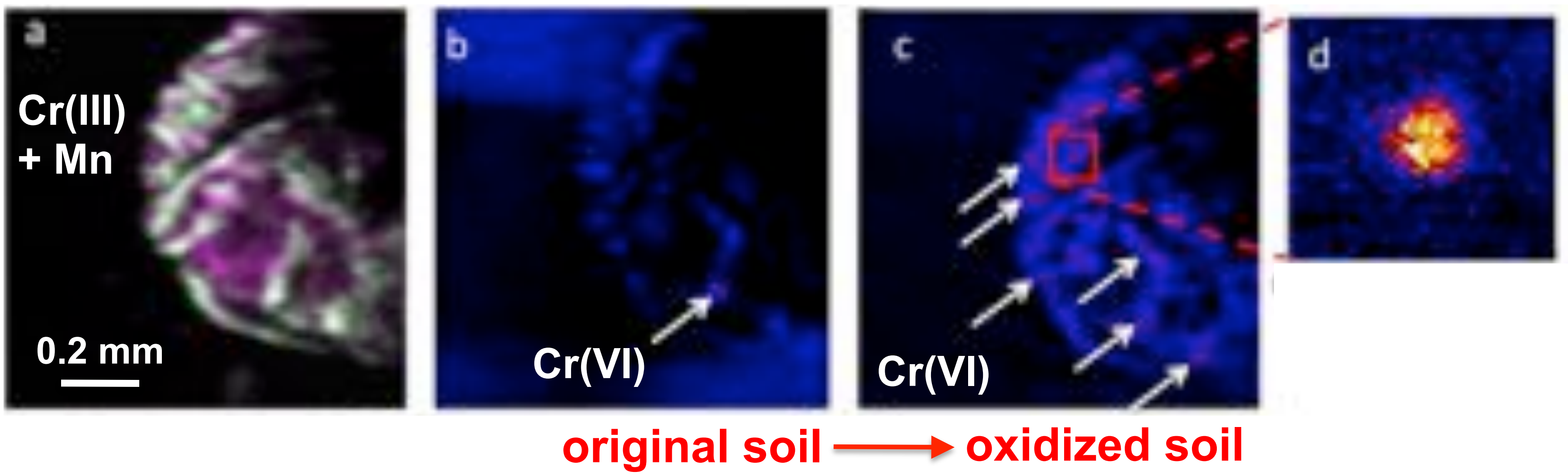
Simple correlation



NSLS Beamline X27A (10 x 10 μm resolution)

MICROSCALE CHEMICAL REACTIVITY

Cr(III) oxidation to Cr(VI) by H_2O_2 is not uniform.
Is it related to geochemical microenvironments?

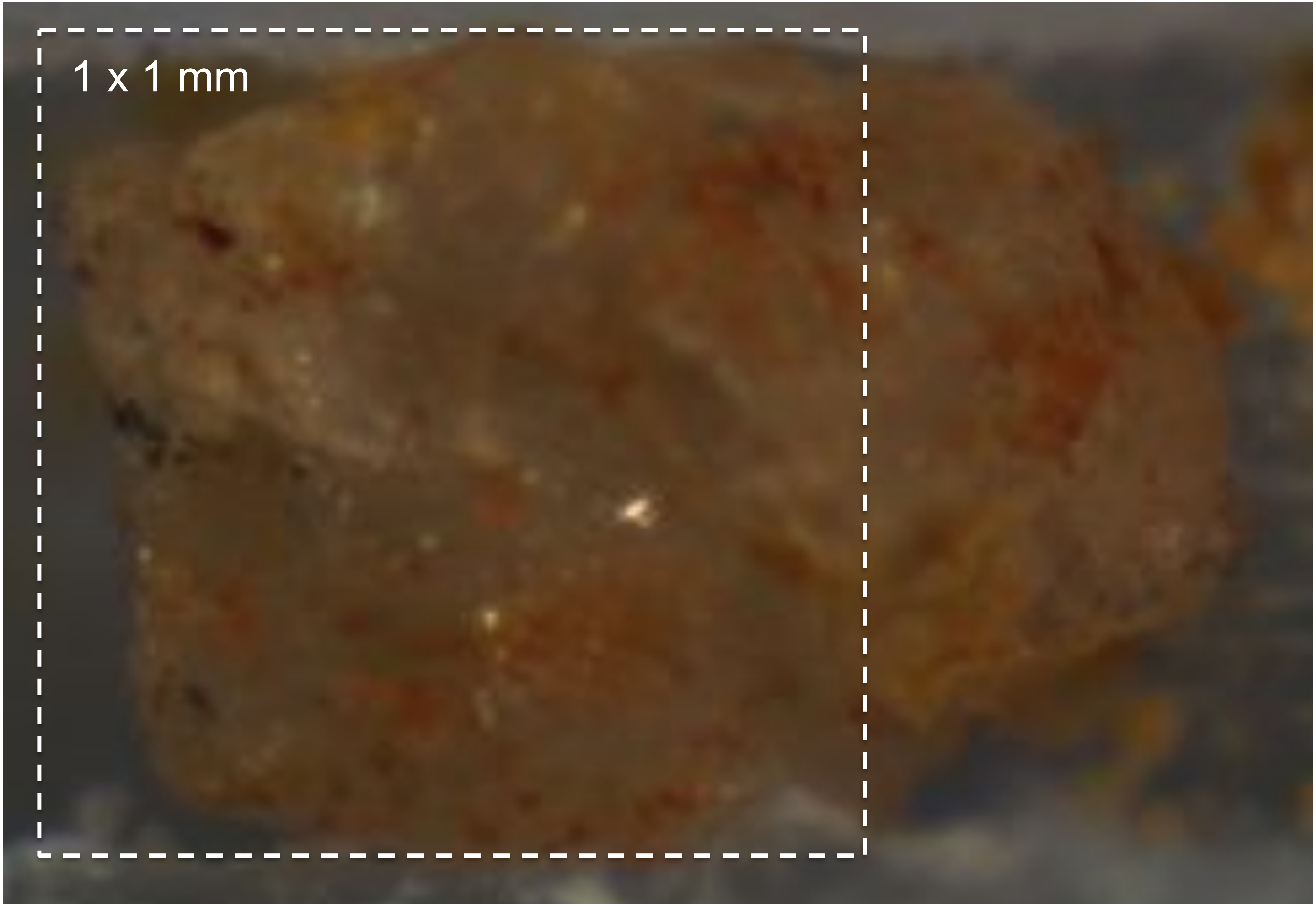


NSLS Beamline X27A (10 x 10 μm resolution)

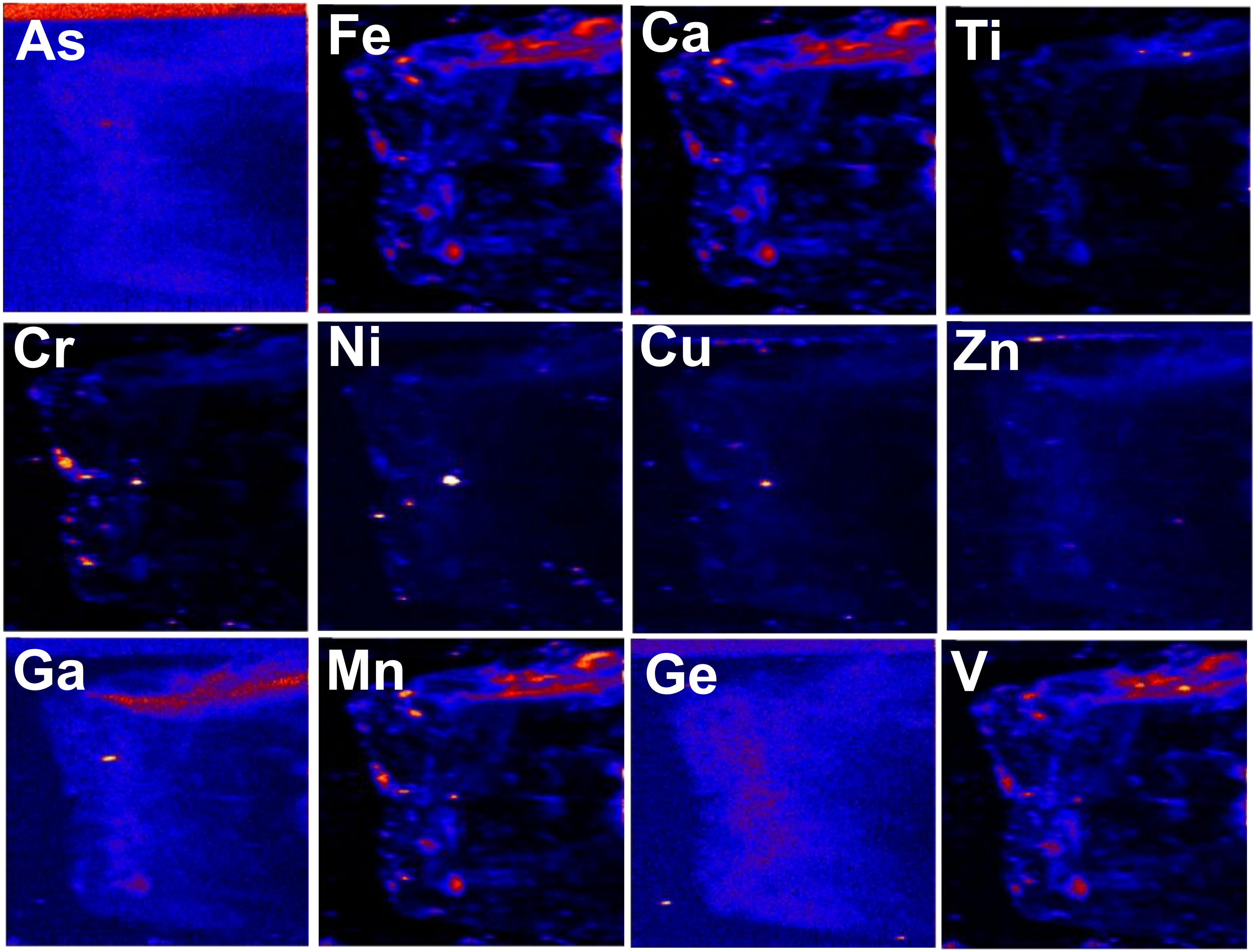
EXAMPLE

ARSENIC ACCUMULATION IN SOIL SAND GRAIN COATINGS TREATED WITH ARSENIC(III)

LIGHT MICROSCOPE IMAGE OF SAND GRAIN

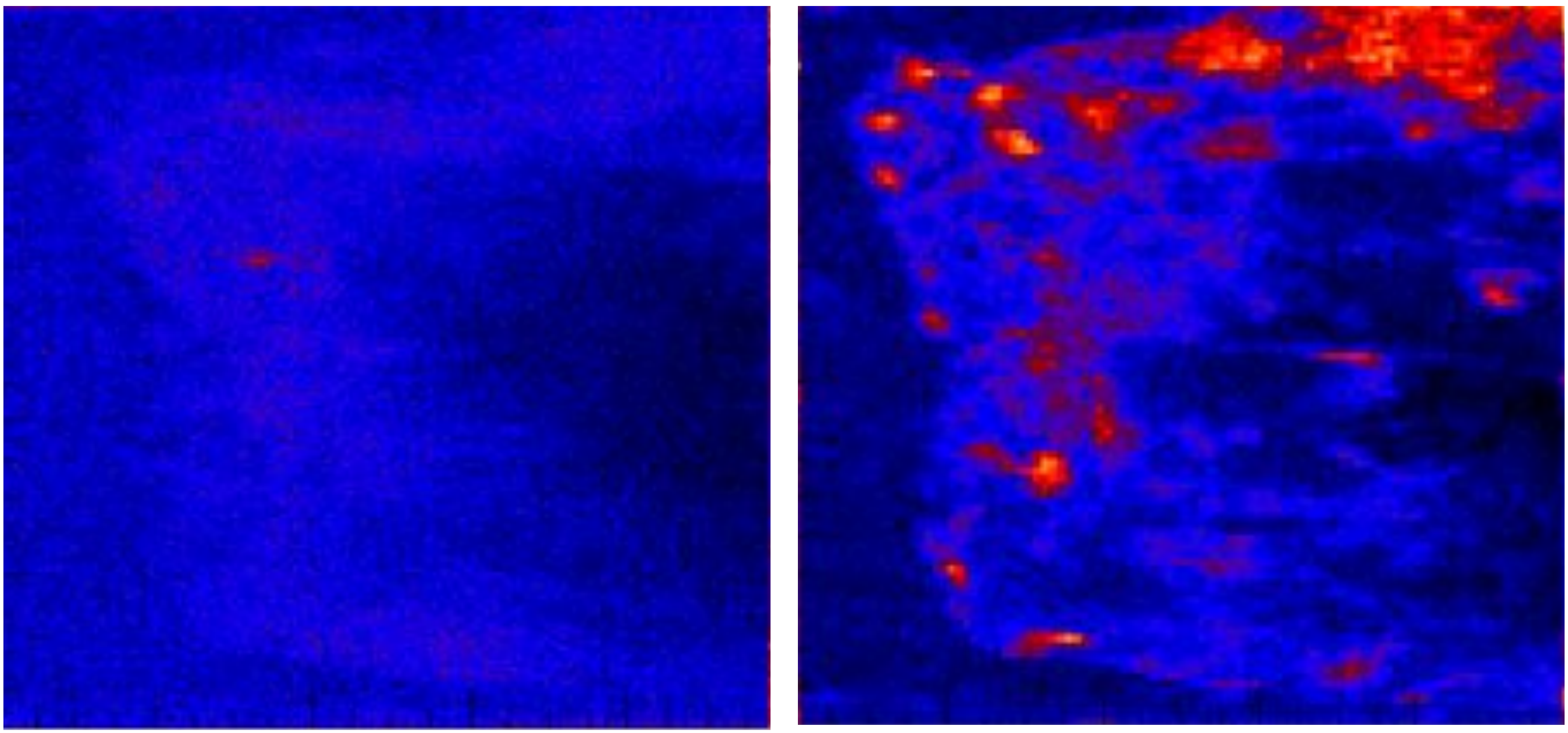


X-ray fluorescence maps (12 keV – 1 x 1 mm^2) from Original Sand Grain



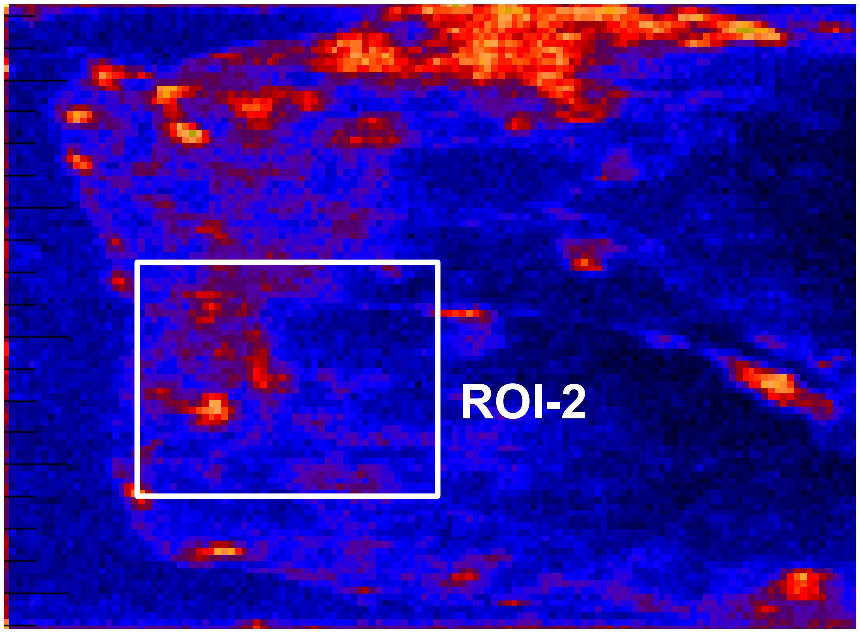
P1E0_6_Nav

Arsenic Distributions before and after treatment with As(III) as 0.1 mM Na_2AsO_2

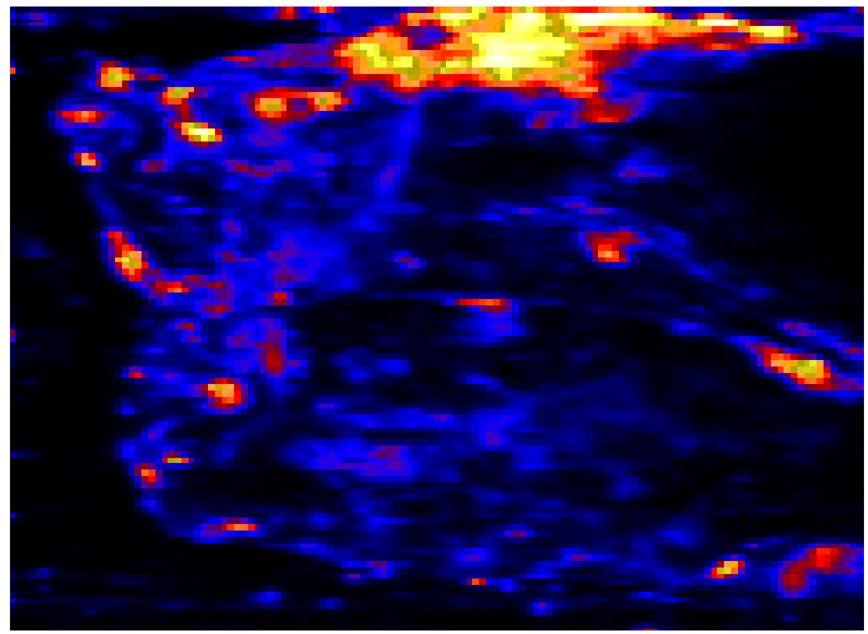


Arsenic distribution is similar to Fe distribution

As (total)

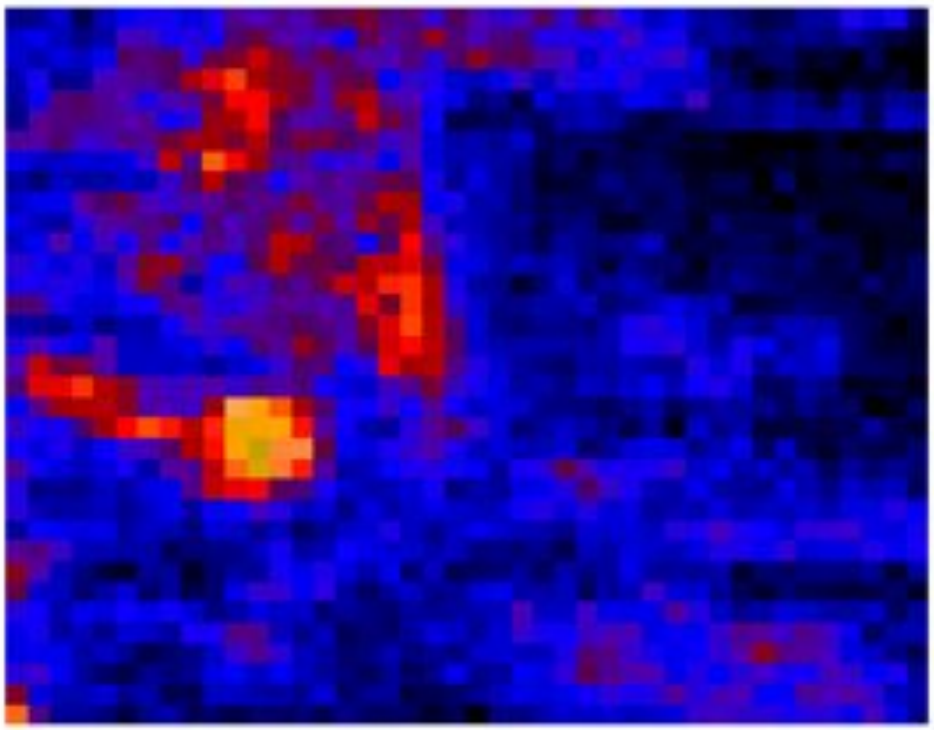


Fe

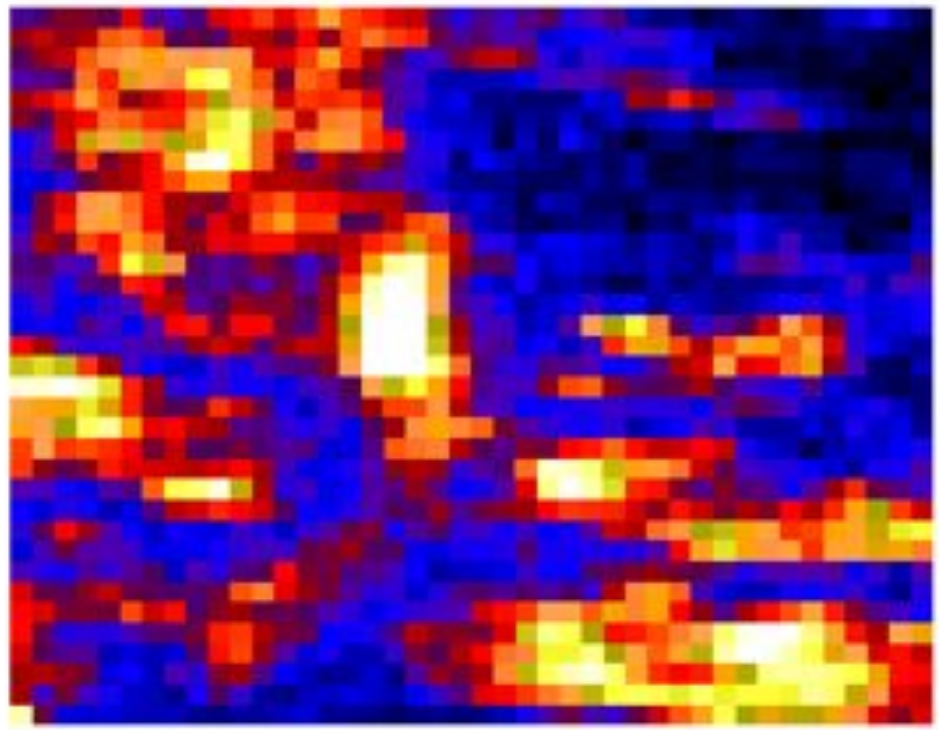


X-ray fluorescence map (12 keV) of ROI-2 after sequential As(III) treatments 1 and 2 (450 x 350 µm image; 10 x 10 um pixels)

After Treatment 1
(0.1 mM $NaAsO_2$ sol'n)

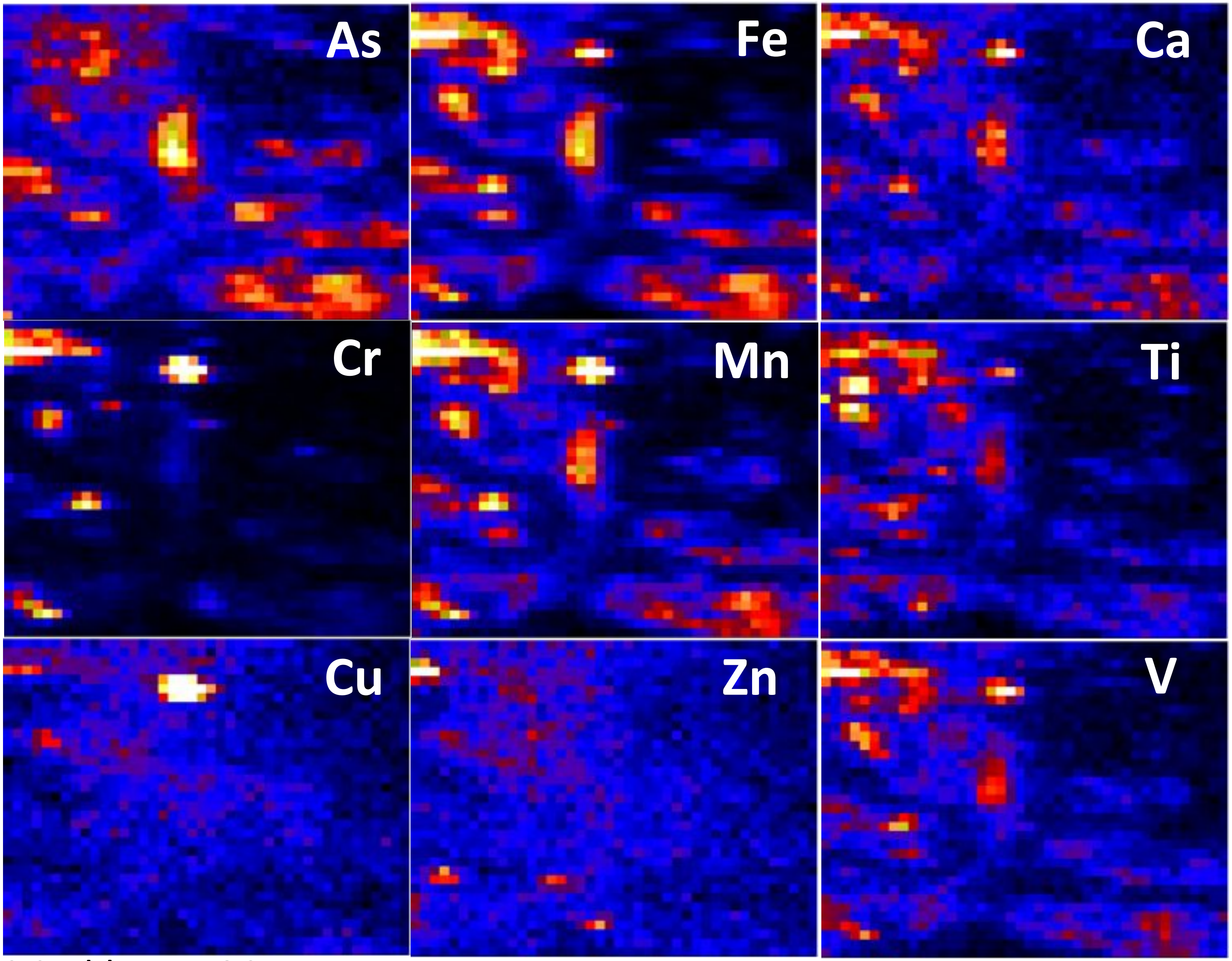


After Treatment 2
(1 mM $NaAsO_2$ sol'n)



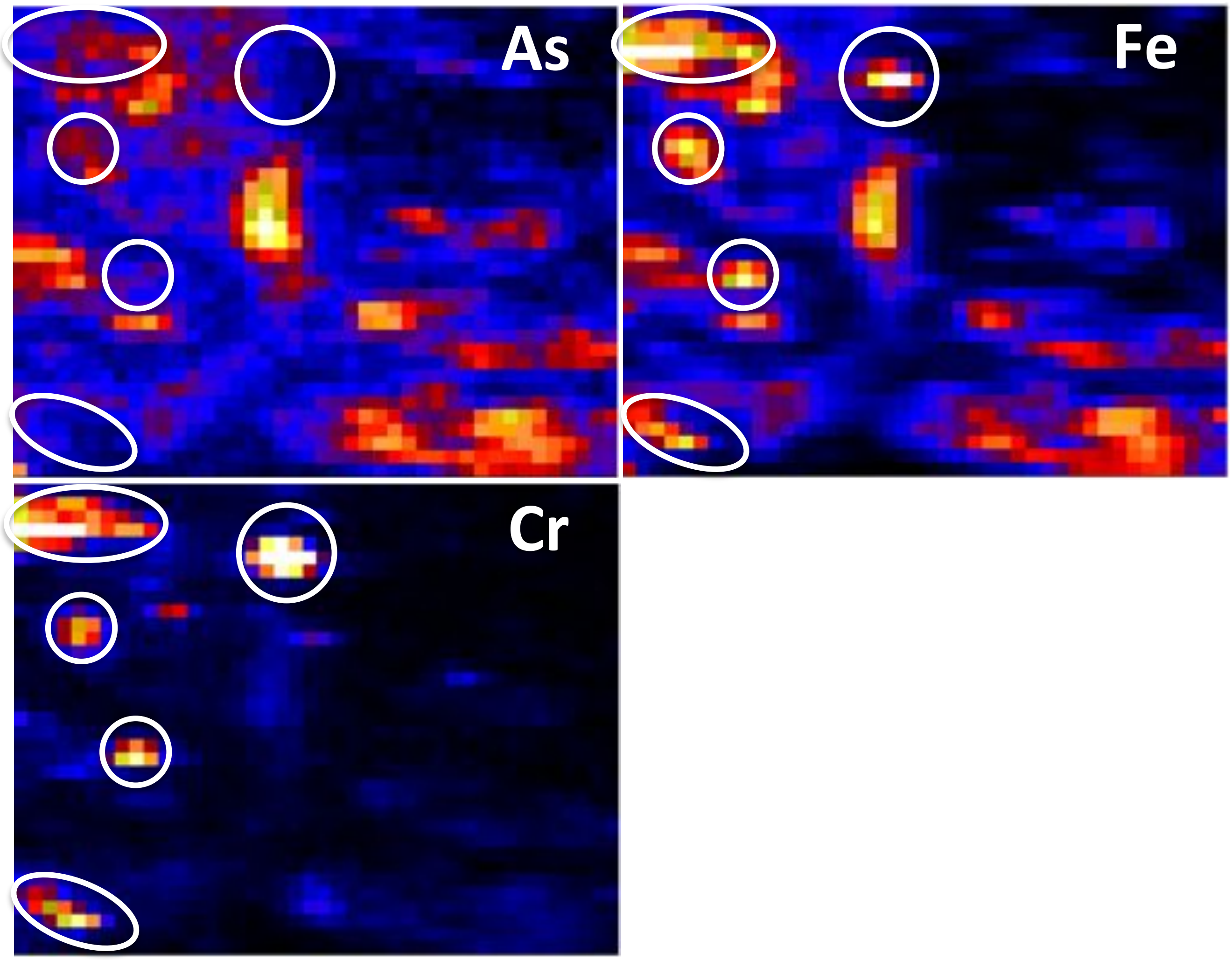
Count range = 84 - 500

Arsenic in ROI-2 after two As(III) treatments



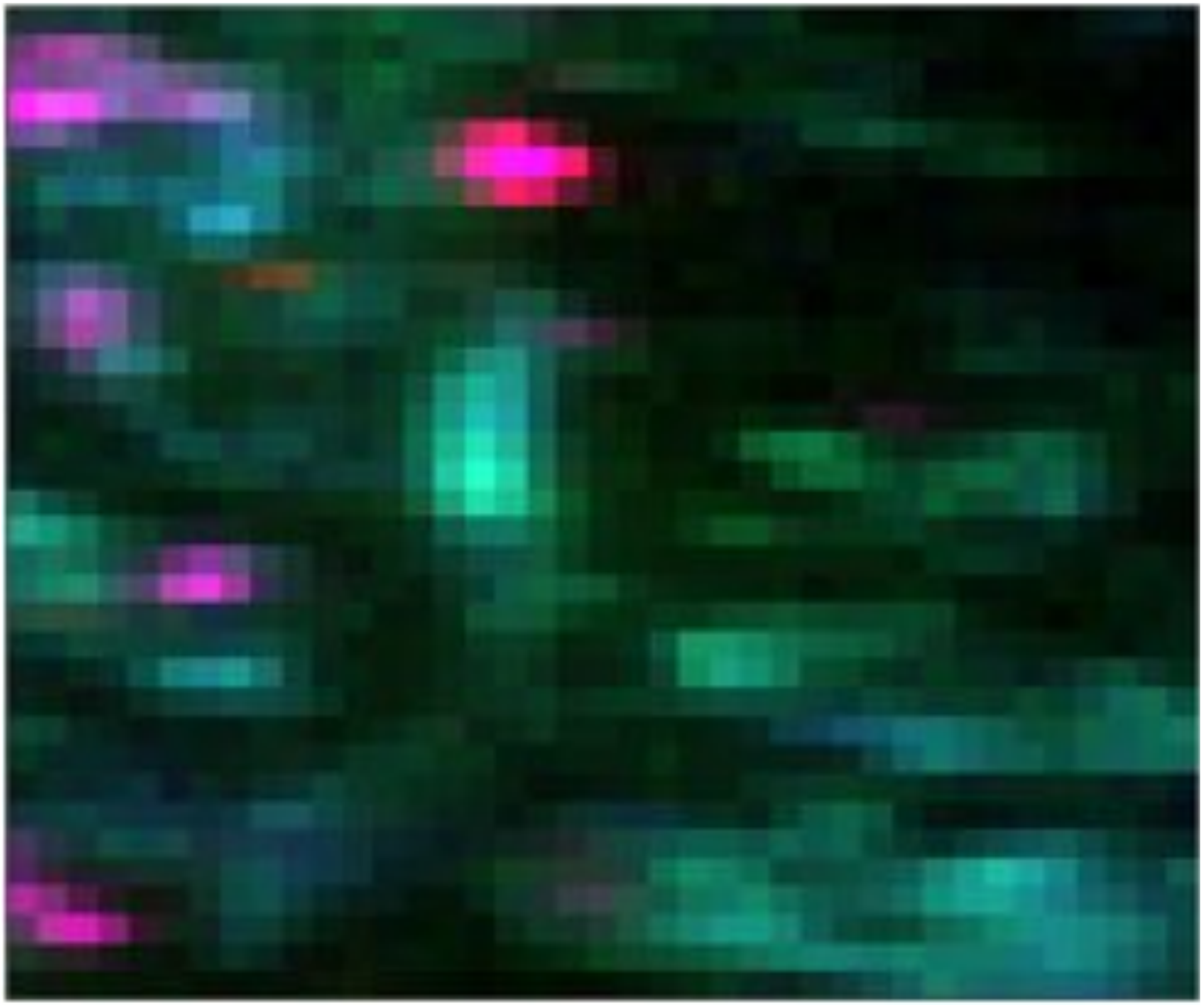
P1E0_6As3_2Rad1b_NAV_ROI2

Arsenic accumulation appears to be diminished in areas of high Cr + high Fe



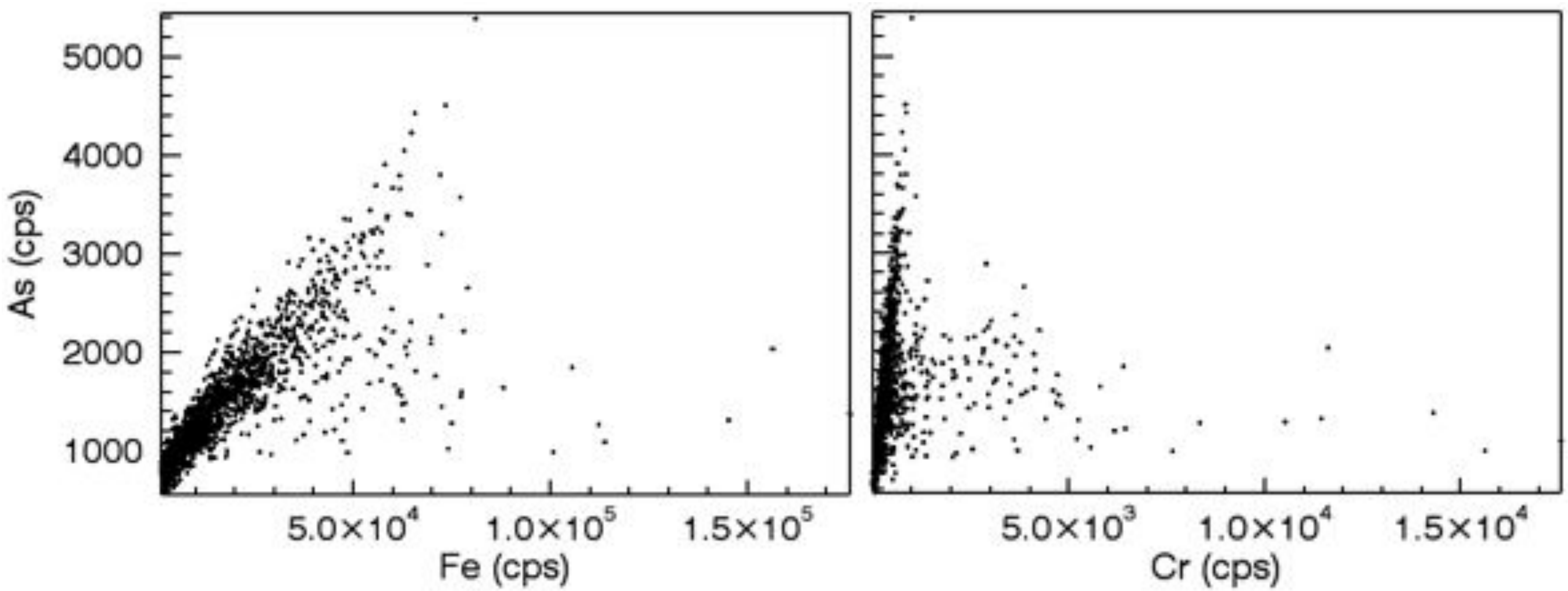
Color blended map with Cr (red), As (green), and Fe (blue)

Purplish: Fe +Cr Orangish: Cr + As (lower Fe) Bluish-green: Fe +As



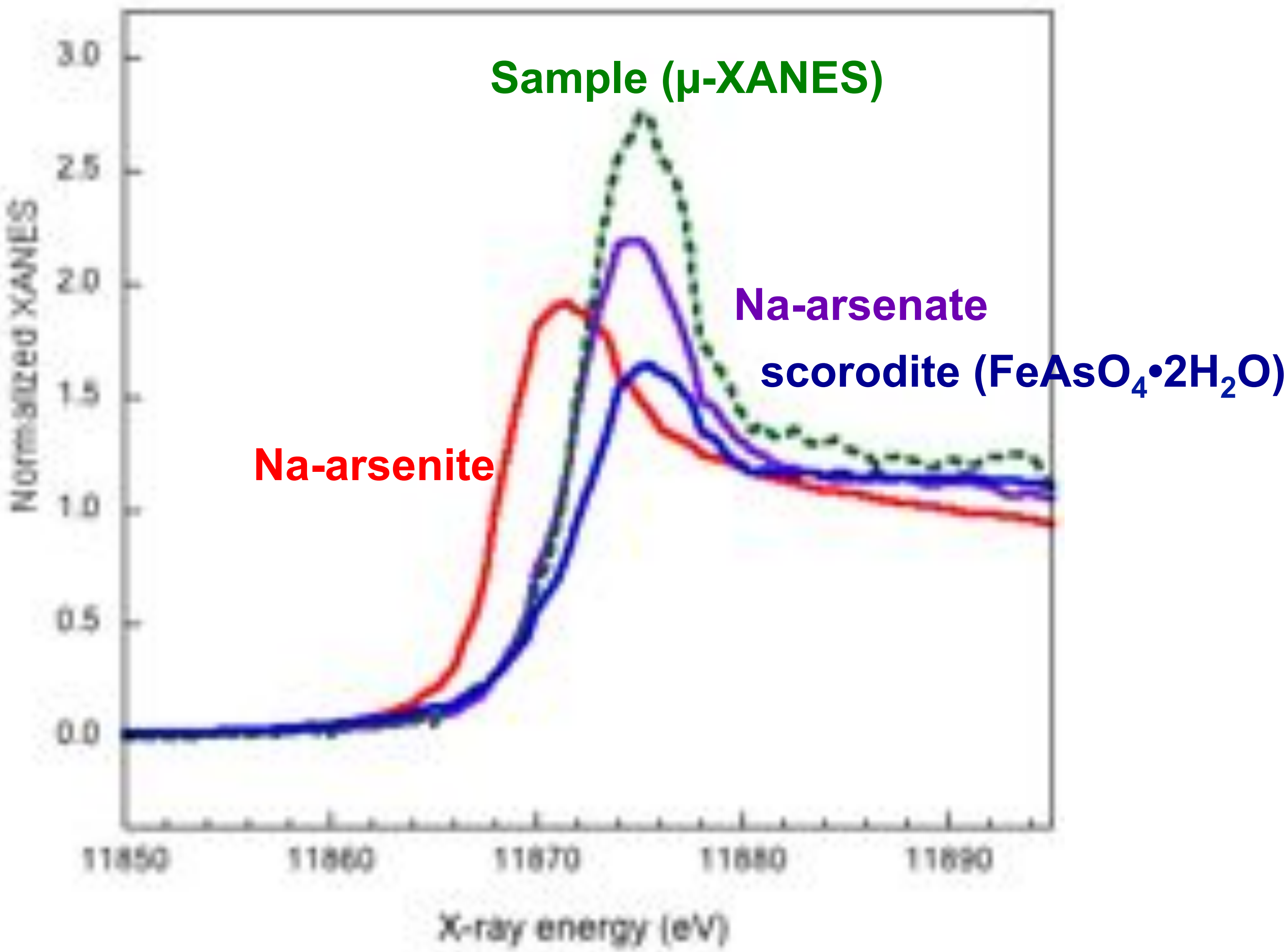
P1E0_6As3_2Rad1b_NAV_ROI2

Simple correlation plots of As vs. Cr or Fe in ROI-2

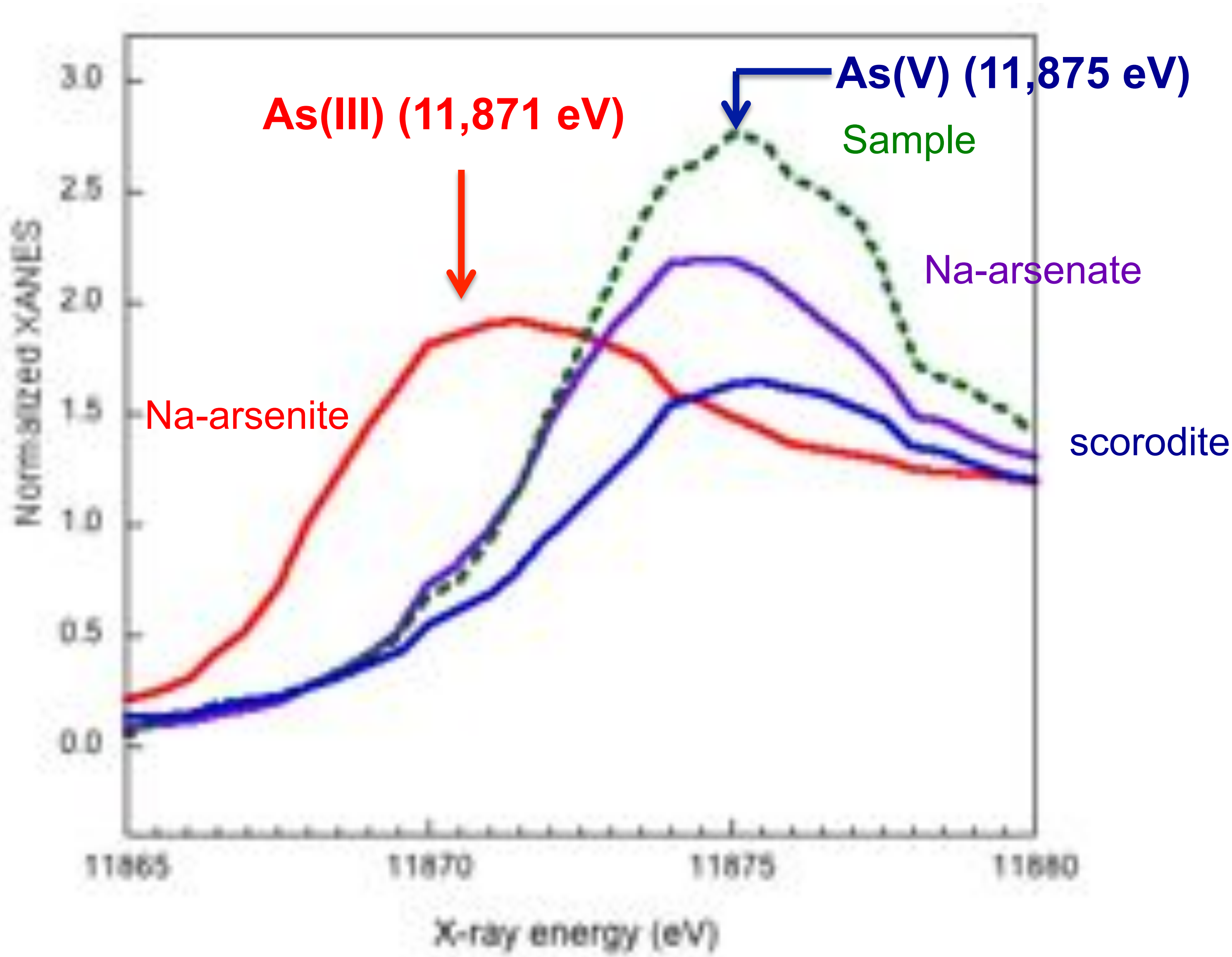


P1E0_6As3_2Rad1b_NAV_ROI2

Selected As K-edge micro-XANES spectra (after 1st As treatment) indicated that As(III) largely oxidized to As(V)



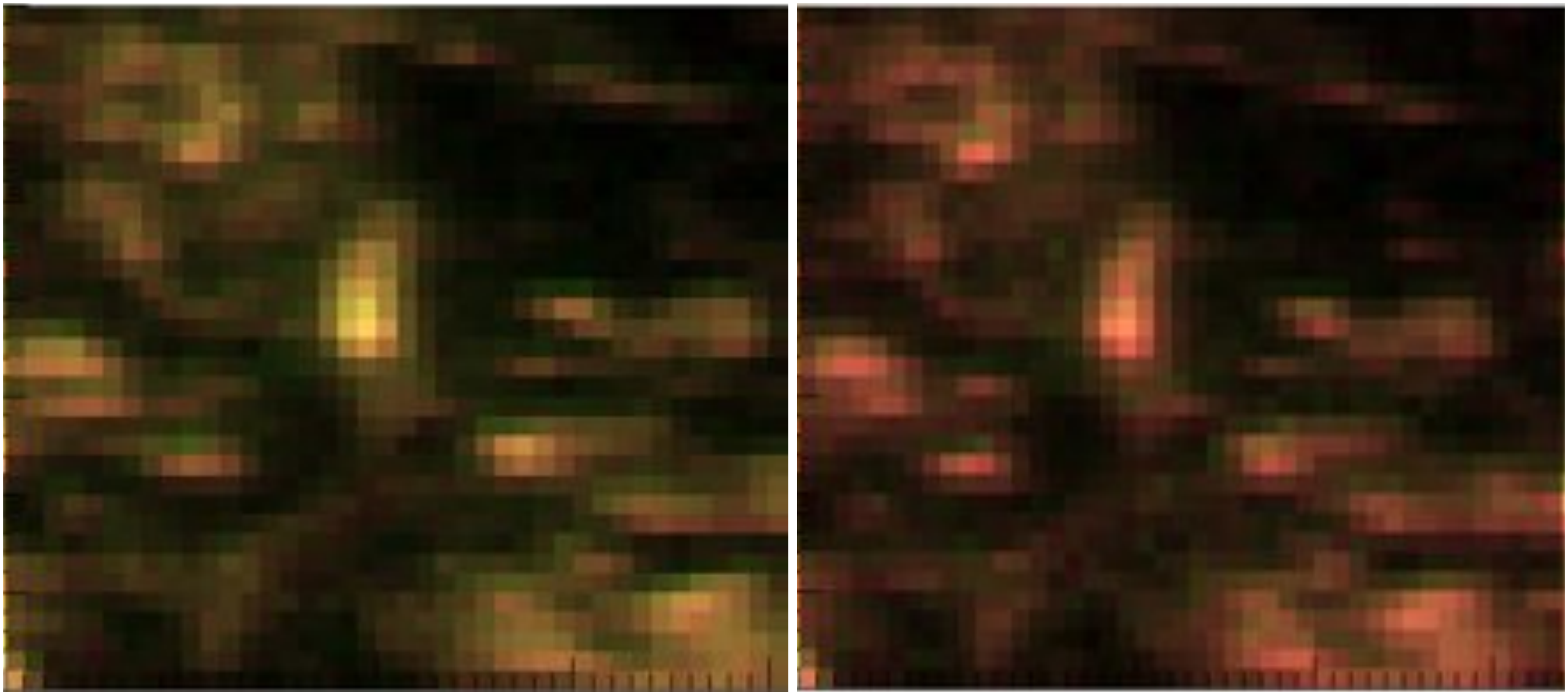
XANES maps collected over larger area, but narrower energy range after 2nd As(III) treatment



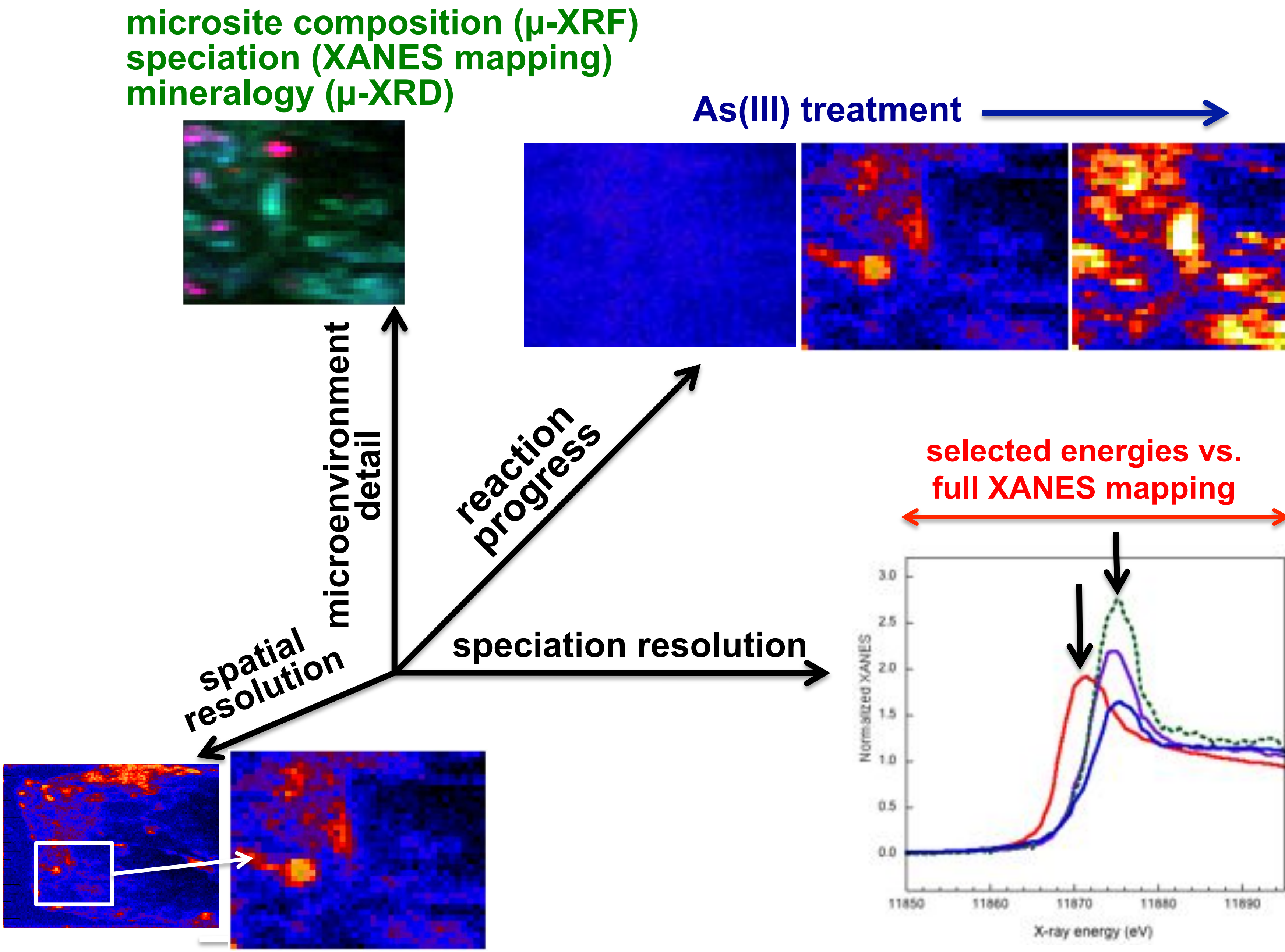
Evidence for UV-visible light-induced oxidation of As(III) to As(V) (1 hour radiation treatment of wet sample)

As(III) = Green + Blue   As(V) = Red

BEFORE   **AFTER**



NEED TO EXPAND AND OPTIMIZE CHARACTERIZATION PARAMETERS



ADVANTAGES OF THE XRS FOR MICROREACTIVITY RESEARCH – IN PRIORITY ORDER

1. VARIABLE SPATIAL RESOLUTION

SURVEY (high flux) and DETAIL (high resolution)

- Can we get stronger element correlations with greater resolution?

2. WIDE ENERGY RANGE (in conjunction with XFN)

As ---> Fe, Mn, S, C (+Al and other trace elements)

Cr ---> Mn, Fe, S, C (+ Fe, Al and other trace elements)

3. HIGH FLUX

Need faster XANES mapping of low-concentration elements

4. X-RAY MICRODIFFRACTION CAPABILITIES

What structures contain the elements that affect transformations?

5. X-RAY TOMOGRAPHY

Can thickness of grain coatings on particles be measured?

NC STATE University

ACKNOWLEDGMENTS

- Ms. Kimberly Hutchison (NC State – Soil Sci.)
- Dr. Martine Duff (Savannah River Site)
- Dr. Joe B. Dixon (Texas A&M)
- Dr. Michael J. Vepraskas (NC State – Soil Sci.)
- Beamline X-27A at the National Synchrotron Light Source and 2-IDB at the Advanced Photon Source,supported by DOE's Divisions of Materials Science and Chemical Sciences